Liquid Desiccant and its Application for Pipeline Drying

by

Syed Younus Ahmed

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

MECHANICAL ENGINEERING

May, 1997

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This thesis, written by

Syed Younus Ahmed

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MASTER OF SCIENCE IN MECHANICAL ENGINEERING

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Date: 6-7-97

Dedicated to

My

PARENTS,

SISTERS

and

BROTHERS

whose patience and perseverance

led me to this accomplishment.

Acknowledgments

In the name of Allah, Most Gracious, Most Merciful

"Read in the name of thy Lord and Cherisher, who created. Created man from a [leech-like] clot. Read and thy Lord is Most Bountiful. He Who taught [the use] of the pen. Taught man that which he knew not. Nay, but man doth transgress all bounds. In that he looketh upon himself as self-sufficient. Verily, to thy Lord is the return [of all]" (The Holy Quran, Surah 96)

All praise and glory be to Almighty Allah (SWT) who gave me courage and patience to carry out this work, and peace and blessings of Allah be upon Prophet Muhammad (PBUH). Acknowledge is due to King Fahd University of Petroleum and Minerals for providing support for this research.

My deep appreciation goes to my thesis advisor Dr.P. Gandhidasan, for his constant help, guidance and the countless hours of attention he devoted throughout the course of this work. He was always kind, understanding and sympathetic to me.

Thanks are also due to my thesis committee members Dr.A.A.Al-Farayedhi and Dr.Ahmet Z. Sahin for their interest, cooperation, advice and constructive criticism.

Special thanks are due to my colleagues and friends for their help and encouragement. They have made my stay at KFUPM a very pleasant and unforgettable experience.

I am also indebted to the department Chairman Dr. M. O. Budair and other faculty members for their support.

Finally, my heartfelt thanks and gratefulness to my parents and other family members for their encouragement and moral support.

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Abstract

Name: Syed Younus Ahmed

Title: Liquid Desiccant and its Application for Pipeline Drying

Major Field: Mechanical Engineering

Date of Degree: May 1997

Liquid desiccants are widely used for dehumidification of air. In order to analyze the performance of the system using desiccant technology, the thermophysical properties of desiccants are essential. In particular, the vapor pressure of the liquid desiccant is one of the important properties in dehumidification. Classical thermodynamic approach is used to predict the vapor pressure of lithium chloride at different concentrations. Simple mixing rules are then used to predict the vapor pressure, density and viscosity of the desiccant mixture namely calcium chloride and lithium chloride.

Drying of petroleum transmission pipelines involves passing of dehumidified air with a certain initial water vapor concentration until the air attains saturation level. For this drying problem, the governing equations are derived and solved analytically as well as numerically with appropriate boundary conditions for the variation of dry air concentration and the drying time.

Liquid desiccant used for dehumidification has to be reconcentrated for reuse. Instead of using thermal energy, a method is proposed in this thesis to use mechanical energy for regeneration. Osmotic pressure required to regenerate the weak desiccant for a given concentration is predicted. Correlations for predicting the pressure required for regenerating the weak desiccant are also developed for different operating parameters.

Master of Science Degree

King Fahd University of Petroleum and Minerals

Dhahran, Saudi Arabia

May 1997

خلاصة الرسالـــة

الاســم : سيد يونس أحمد
عنوان الرساله : مواد التجفيف السائله وتطبيقاتها في تجفيف خطوط الانابيب
المجال الرئيسي : الهندسه الميكانيكيه
تاريـخ الدرجه : مايو ١٩٩٧ م

تستخدم مواد التجفيف السائله بشكل كبير في إزالة الرطوبه من الهواء . وتجب معرفة الخواص الفيزيائيه لهذه المواد حتى يمكن تحليل الانظمه التي تعتمدها .

يعتبر الضغط البخاري أحد هذه الخصائص المهمه . وتستخدم الديناميكا الحراريه التقليديه للتنبؤ بالضغط البخاري لماده كلوريد الليثيوم عند درجات تركيز مختلفه وبعد ذلك تطبق علاقات الخلط البسيطه للتنبؤ بالضغط البخاري ، الكثافه ودرجة اللزوجه لكل من كلوريد الكالسيوم وكلوريد الليثيوم .

ويلزم لتبريه خطوط انابيب البترول مرور هواء مجفف ذو تركيز معين من بخار الماء حتى يصل الى درجة التشبع . وقد تم استنباط المعادلات التى تحكم عملية التجفيف المذكوره وتم حلها تحليليا ورقميا آخذين في الاعتبار الحالات عند الحدود والتغير في تركيز الهواء الجاف مع مرور الوقت .

وتوصى الدراسه بإعادة التركيز على استخدام مواد التجفيف السائله فبدلاً من استخدام الطاقه الحراريه تم اقتراح طريقه في هذه الدراسه لاستخدام الطاقه الميكانيكيه المتجدده . وتم التنبؤ بقيم الضغط الانتشاري المطلوب لاسترجاع المجفف . وقد تم ايضا استنباط علاقات يمكن استخدامها للتنبؤ بالضغط المطلوب لتجديد المجفف تحت ظروف تشغيل مختلفه

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران – المملكه العربيه السعوديه
مايو ١٩٩٧ م

Nomenclature

A	pipeline cross section area, m^2
$A1$	constant
a_1	constant
b_1	constant
B , C , D	second, third, and forth coefficient of Virial equation
D	pipeline diameter in chapter 5, m
D_{va}	diffusion coefficient
C^*	concentration of water vapor in dry air, kg of dry air/kg of water
$\frac{C_A}{C}$	mole fraction concentration
C^*_{sat}	concentration of water vapor in dry air at saturation, kg of water/kg of dry air
C^*_o	concentration of water vapor in dry air at inlet, kg of water/kg of dry air
f	fugacity
E	any property
F	helmholtz function
F	mass transfer coefficient in chapter 5, kg/m^2s
g	gibbs energy at constant temperature, J

G	gibbs energy, J
h	convection coefficient from air to water, W/m^2K
h	spatial step used in chapter 5
I	interaction parameter, as given in eqn.(4.4)
k	mass transfer coefficient, kg/m^2s
L	length of pipeline, m
m	time step
MW_v	molecular weight of vapor
MW_a	molecular weight of air
n	number of moles, number of components in chapter 3
N_A	evaporation rate per unit area, kg/m^2s
N_B	evaporation rate per unit area, kg/m^2s
N	total number of moles
p	partial pressure, $mm\ Hg$
P	pressure, $mm\ Hg$
Q	flow rate, kg/s
R	gas constant, $atm\ cm^3\ /g\ mol\ K$
Re	Reynolds number
s	specific entropy, J/kgK
S	entropy, J/kgK

t	time, s
T	temperature, ^oC or K
T_a	ambient air temperature, ^oC or K
T_e	entrance temperature of pipeline, ^oC or K
T_{dp}	dew point temperature, ^oC or K
u	specific internal energy, J/kg
U	total internal energy, J/kg
$U1$	some function
v	specific volume, m^3/kg
$\overline{v}_i$	specific molar volume, m^3/kg
$\overline{V}$	velocity of dry air used in chapter 5, m/s
V	total volume, m^3
W	amount of water per unit length of pipe, kg/m
W_o	initial amount of water per unit length of pipe, kg/m
x	spatial variable, m
x_i	mole fraction for the component i
x_l	mole fraction in the liquid phase
y	mole fraction in the gas phase
Y	mole fraction concentration
Y_{sat}	mole fraction concentration at saturation

z	compressibility factor

Superscript

l	liquid
m	constant
n	constant
o	at reference state
sat	saturation
v	vapor
1, 2, 3, m	phases

Subscript

a, b	constituents
ha	humid air
id	ideal
ref	reference state
i, j, k	components, inlet in chapter 5
mix	mixture
o	outlet
$pure$	pure component
1	component 1
2	component 2

3	component 3
11, 22	between same component
12	between two different components

Greek

α, β, π	phases
α_1, β_1	constants used in chapter 5
β	mass transfer coefficient between solution film and air stream, $kg/h\ m^2\ (mmHg)$ used in chapter 5
γ	activity coefficient used in eqn (3.27)
ζ	interaction constant for air-water vapor system, as given in eqn (3.55)
μ	chemical potential
μ_T	chemical potential at constant temperature
ρ	density, kg/m^3
φ	fugacity coefficient
ψ	weight fraction or volume fraction of a constituent
δ	constant
ω	constant
μ_i^{π}	reference value
$\mu_{i,o}^{\pi}$	reference value of pure liquid
σ	constant

ν	dynamic viscosity, kg/ms
η	kinematic viscosity, m^2/s
Π	osmotic pressure, MPa

Chapter 1

Introduction

1.1 Drying

Drying is a common everyday activity which has its origins in antiquity. In medieval physiology, dryness was one of the fundamental qualities of elements. Considerable quantities of heat are used to dry moist materials of various kinds in numerous industries. Because of this enormous diversity of applications, a theoretical understanding of the drying behavior of industrial equipment has been slow to mature. Only recently has the literature provided means whereby relatively simple, but effective, analysis can be undertaken as a basis for the design and operation of a drying plant. The varied nature and history of drying operations have begotten a wealth of dryer types. Some operations are long- standing, such as the drying of fellmongered and scoured wool: other techniques are recent innovations, as, for example, in the

preparation of ore concentrates from mineral slurries by spray drying. A number of attempts have been made to classify the dryers and drying processes. The most commonly used drying methods are:

1. Convection
2. Conduction
3. Radiation
4. Dielectric heating
5. Drying by dehumidified air.

The last process in the list that is, drying by dehumidified or dry air is considered to be the most economical and environmental friendly. Dehumidification technology is suited to a wide variety of demanding applications.

1.2 Uses of Dry Air

The uses of dry air are almost as limitless as the ingenuity of man. However, these uses normally fall into four general areas: storage, production, packaging and process.

1.2.1 Storage

In storage applications, the storage space is maintained at a specific relative humidity and sometimes temperature as well, so that the products in storage cannot adsorb moisture from the surrounding atmosphere, or so that the products are protected from corrosion. At relative humidities below 30%, oxidation of steel is virtually nonexistent. At levels between 30 to 60 %, oxidation occurs slowly. Above 60 %, a marked increase in the rate of corrosion by oxidation occurs. For this reason, dehumidification has been used in several industries to prevent corrosion of equipment. Another example of this is a water pumping station or sewage plant, where the prime humidity control problem is the maintenance of a dew point within the space which is lower than the temperature of the water which is being circulated or stored there. In this way, condensation of moisture on the outside of pumps and piping is eliminated. Application of dry air is important in the food industry, where rations or nuts are stored at near freezing temperatures or even below freezing temperatures, and the humidity must be kept low at the same time to avoid the formation of mold, the deterioration of the product, and the deterioration of the packaging that contains the product. Hygroscopic materials such as sugar, flour, plastics, and other types of synthetic material are often stored in humidity controlled areas.

1.2.2 Production

The uses of dry air in production operations are infinite. Here an atmosphere beneficial to the particular operation is being obtained by dehumidification. In most cases, temperature is controlled at the same time, but there are times when the product being handled is not responsive to temperature. Some of the common production applications are in the food and drug industries, such as the candy industry where the hard sugar candy may become sticky and adhere to dies and packaging materials, thus slowing down production. In the drug industry, many of the modern discoveries cannot be mixed, packaged or compounded except in extremely dry atmospheres. In the food industry, powdery products such as flour, cocoa, concentrates, etc. are almost impossible to handle in areas where the moisture content of the air is not carefully controlled. In electronic industry, moisture can cause a multitude of problems ranging from pitting of electrical contacts due to excessive arcing under high humidity conditions to the bursting of casings on electrical heating elements if moisture is sealed into the casing during manufacture.

1.2.3 Packaging

Packaging operations offer a unique application for the use of dry air. Food stuffs, such as potato chips, soda crackers, soup concentrates, instant coffee and other extremely hygroscopic materials require only a very small amount of water vapor to

cause them to congeal or become rancid and stale after a very short period of time. The use of dry air in the packaging area to insure that dry air is packaged with the product insures that the product cannot adsorb the small amount of moisture. The humidity requirements for a packaging area are normally dependent upon the physical characteristics of the product itself. The main purpose is to control the moisture content of the material being packaged so that it does not deteriorate packaging, during transit to the end user.

1.2.4 Process

The uses of dry air in process applications are varied and difficult to separate into specific categories. The division between production applications and process applications is rather fine. By the term process air, we usually mean the use of an air stream with a specific dew point for a specific purpose. One example might be the use of an air stream at 18 ^oC dew point over a die or roller which is cooled with water. If this die is used to mold plastics, any water on the surface of the die will ruin the surface of the plastic product. Another application might be the use of a warm dry air stream passing over a cold product entering into a warm humid space to prevent the formation of condensation upon the cool surface. Yet another example would be the use of a warm dry air stream directed through fluorescent tubes to assist in the drying of the fluorescent coating without any possible regain of moisture.

1.3 Dehumidification of Air

Dehumidification technology is suited to a wide variety of engineering applications. Recent developments in dehumidification system design allow plant engineers to solve process and environmental problems. There are three common ways of accomplishing this.

1.3.1 Refrigeration Process

The first and most common method is the reduction of moisture in the air by means of reducing the temperature using refrigeration. By examination of the dew point line or saturation curve on the psychrometric chart, it can be seen that as the temperature of the air is lowered, the amount of moisture which it can hold is reduced considerably. Thus, by cooling the air below the dew point of the moisture contained in that air, we can condense out and remove some of the moisture vapor in the liquid form. The reduction in air temperature is also limited by the freezing point of the water condensing on the cooling coil. So, if air with very low moisture content is required, the refrigeration process becomes complicated and involves the use of dual cooling coils and a defrost cycle or brine spray system. The increase in power normally required in refrigeration equipment operating at low suction pressures also makes this approach costly.

1.3.2 Air Compression

Air compression constitutes another method of reducing the moisture content in air. When air is compressed, the partial pressure of the water vapor in the water-gas mixture is raised to the point where moisture can be condensed from the air at a higher temperature. This approach is sometimes quite practical for very small volumes of air to be dehumidified. But the cost of compression equipment, the high power requirements and the amount of cooling water required for after-cooling make it very impractical for large volumes of air.

1.3.3 Desiccant Dehumidification

The third and most simple method of obtaining dry air is through the use of desiccant dehumidifiers. These dehumidifiers utilize solid and liquid desiccants which have an enormous natural affinity for water. This thesis deals with this process for dehumidification of air for drying purposes because, extremely low dew points can be obtained in this way without the need of complex systems or controls.

1.4 Desiccants

Materials which have the tendency to attract and hold the water vapor are termed as desiccants. A commercial desiccant takes up between 10 and 1100% of its dry weight in water vapor, depending on its type and the moisture available in the environment

[1]. Further commercial desiccants continue to attract moisture even when the surrounding air is quite dry, a characteristic which other materials do not share. All desiccants behave in a similar manner i.e., they attract moisture until they reach equilibrium with the surrounding air. Moisture is usually removed from the desiccant by heating it to temperatures between 50 and 250 ^oC and exposing it to a scavenger airstream. After the desiccant dries it must be cooled so that it can attract moisture once again. Sorption (absorption in case of liquid desiccants and adsorption in case of solid desiccants) always generates sensible heat equal to the latent heat of the water vapor taken up by the desiccant, plus an additional heat of sorption that carries between 5 and 25% of the latent heat of the water vapor. This heat is transferred to the desiccant and the surrounding air. The process of attracting and holding moisture is described as absorption or adsorption, depending whether the desiccant undergoes a chemical change as it takes on moisture. Adsorption does change the desiccant except by the addition of the weight of water vapor. Absorption, on the other hand, changes from a solid to a liquid as it absorbs moisture.

1.5 Desiccant Classification

Desiccants can be solids or liquids and can hold moisture through adsorption or absorption. Most absorbents are liquids, and most adsorbents are solids. Adsorbents are solid material with a tremendous internal surface area per unit of mass, a single

gram can have more than 4600 m^2 of surface area [1]. The bulk of the adsorbed water is contained by condensation into the capillaries, and the majority of the surface area that attracts individual water molecules is in the crystalline structure of the material itself. Adsorbents attract moisture because of the electric field at the desiccant surface. The field is not uniform in either force or charge, so it attracts water molecules that have a net opposite charge from specific sites on the desiccant surface. When the complete surface is covered, the adsorbent can hold still more moisture as vapor condenses into the first layer and fills the capillaries throughout the material.

General classes of solid desiccants are,

1. Silica Gels
2. Zeolites
3. Activated Aluminas
4. Carbons

In standard practice, the behavior of a liquid desiccant can be controlled by adjusting its concentration, its temperature, or both. Concentration is controlled by heating the desiccant to drive moisture out into a waste airstream or directly to the ambient. Commercially available liquid desiccants have an especially high water holding capacity. Each molecule of lithium chloride, for example, can hold two water

molecules even in dry state. Above two water molecules per molecule of LiCl, the desiccant becomes a liquid and continues to absorb moisture. If the solution is in equilibrium with air at a 90% relative humidity condition, approximately 26 water molecules are attached to each molecule of LiCl. This represents a water absorption of more than 1000% on a dry weight basis [1]. As a practical matter, however, the absorption process is limited by the surface area of a desiccant exposed to the air being dehumidified and the contact time allowed for the reaction. More surface area and more contact time allows the desiccant to approach its theoretical capacity.

Commercial desiccant systems reflect these realities either by spraying the desiccant onto an extended surface much like in a cooling tower, or holding a solution in a rotating extended surface with a large solution capacity. Thus a liquid desiccant dehumidifier contacts air with a liquid desiccant solution. The liquid has a vapor pressure lower than water at the same temperature, and the air passing over the solution approaches this reduced vapor pressure; it is dehumidified. The vapor pressure of a liquid desiccant solution is directly proportional to its temperature and inversely proportional to its concentration [2]. As the desiccant content in the mixture increases, its vapor pressure decreases. This pressure difference allows the desiccant solution to absorb moisture from the air whenever the vapor pressure of the air is greater than that of the solution. In the present research work, liquid desiccants have been chosen for the process of dehumidification due to the following advantages:

1. Liquid desiccants are readily circulated by means of a small pump and dispersed over packings to insure a large surface area of exposure without great pressure drops in the gas stream.

2. The regeneration temperature required for these systems is about $50 - 65\ ^{o}C$ and thus any low grade thermal energy can be effectively used for regenerating weak desiccants.

3. Liquid desiccants can be used as a heat transfer medium in heat exchangers and hence it could be precooled or preheated when required.

4. In liquid desiccant systems a part of the weak desiccant can be over-concentrated and mixed with the remaining weak desiccant. Hence, all the weak desiccant need not be circulated for regeneration.

1.6 Regeneration of Liquid Desiccants

Liquid desiccants are widely used to dehumidify air for many industrial and space conditioning applications. Currently available commercial liquid desiccant systems are designed to use fossil fuels to concentrate the weak desiccant solution. For regenerating such solutions only low-grade heat is required and most of the time solar energy is effectively used in such processes. Recently, a few attempts have been made to use liquid desiccants in various industrial and domestic applications,

such as cooling of buildings, power generation, drying and food processing etc. In all these applications an important part of the system is regenerator, in which the weak desiccant solution is concentrated. Different types of solar regenerators are available for regenerating the weak solution such as:

1. Open - type solar regenerator.

2. Fully - closed solar regenerator.

3. Partly - open, partly - closed solar regenerator.

4. Wind forced- flow solar regenerator.

5. Forced-flow solar regenerator.

In the present work, instead of using the conventional processes to regenerate the weak desiccant, an attempt is made to use reverse osmosis (which has been used traditionally for water desalination) for regeneration of weak desiccant solution.

1.7 Pipeline Drying

To verify the integrity of the installation of pipelines, especially in the oil and gas industry, hydrotesting is used. This involves the sealing of the sections of the pipe, filling with water and pressing to check the pipe strength (strength test)and leak tightness (leak test). Most of the water that remains in a pipeline after the hydraulic

test can be removed by successively passing a series of cylindrical or spherical inserts called pigs, through the pipeline is commonly known as pigging operation. This is performed in wet-gas pipelines to periodically remove liquid accumulation in the lower portion of hilly terrain pipelines or the water that sticks to the surface of the pipes. In pigging operation of gas or petroleum pipelines, water inflatable rubber or neoprene spheres are tightly fit and inserted into the pipe at regular time intervals and pushed. As the pig moves, a liquid zone forms and grows by scooping the liquid.

After this operation, a very thin layer of water (usually 100 μm or less than this), still remains on the inside surface of the pipeline. This very thin layer of water present appears a small amount but when the total amount of water for the whole pipeline is calculated usually comes to thousands of kilogram.

It is necessary to dry the inner surface of the pipeline, otherwise hydrates of hydrocarbons may form, resulting in obstruction of the pipes, measurement instruments valves, etc. and hence in failures. In the transportation of jet fuel, the presence of moisture is entirely unacceptable. A special feature of pipelines for pumping carbon dioxide is the need to carefully rid them of water after the hydraulic test, since highly corrosive carbonic acid is formed due to the interaction of carbon dioxide with water. Therefore, before putting the pipeline into operation it has to be dried of the water present after the hydraulic testing.

The main objectives of the present study are to use thermodynamic equilibrium concept to find the vapor pressure of a single desiccant and then, use the mixing rules to determine the properties such as density, viscosity and vapor pressure for the desiccant mixture.

In addition to this the drying behavior of pipeline drying by both analytical as well as numerical approach using dehumidified air will also be studied. Desiccant used for dehumidification of air has to be regenerated for reuse, an analytical study will be conducted to use mechanical energy, instead of thermal energy for regeneration of weak desiccant.

Chapter 2

Literature Review

2.1 Desiccants and Desiccant Mixtures

Many attempts have been made to use liquid desiccants such as lithium bromide, lithium chloride, calcium chloride, triethylene glycol, etc. in solar applications. The selection of a desiccant for particular application depends on the various operating parameters such as boiling point elevation, energy storage density, the regeneration temperature, thermophysical properties, availability, cost, etc. During the early 1980s, desiccant systems emerged from their 50-year old heritage in industrial dehumidification to take a more prominent role in air-conditioning. The results are improved indoor air quality and enhanced occupant comfort. Desiccants are also used to save energy in buildings with high ventilation loads. Hotels use desiccant systems to provide dry makeup air to maintain a slight positive pressure, as forced

humid air infiltration has been identified as a major cause of the mold and mildew problem. Likewise, hospitals have used desiccant systems to dry and cool the outside air in operating rooms [3]. Desiccants can also be used in drying of grains and crops, controlling the ripening of fruits, in storage compartment to prevent corrosion, mildew, fermentation, drying of gases before storage, in energy storage system, concentration of fruit juices and power generation.

Humidity control at low temperature is one of many tasks that desiccants can accomplish very economically. Desiccants attract moisture because of a difference in vapor pressures. A cool, dry desiccant has a very low surface vapor pressure compared to the vapor pressure of humid air. Several experiments and theoretical investigations of thermal systems using single desiccant have been reported [4], [5] and [2]. However, a very few have emphasized the analysis of a thermal system employing a mixture of desiccants [6] and [7]. Among the desiccant candidates possessing the minimum qualification to be considered, desiccant cost is of primary concern. Salts such as calcium chloride and zinc chloride cost much less than salts which have traditionally been used, such as lithium bromide or lithium chloride. Lithium chloride is the most stable liquid desiccant and has large dehydration concentration $30\% - 40\%$ but its cost is relatively high $\$8.00 - \$16.00/kg$ [6]. It is expected that it will reduce the relative humidity by up to 60%. Calcium chloride is the cheapest desiccant which costs about 40 $cents/kg$ and most readily available desiccant, but it has the disadvantage of being unstable depending on the air inlet

conditions and the concentration of the desiccant in the solution.

To use the thermodynamics of equilibrium for the calculation of vapor pressure of the liquid desiccants, the understanding of the fugacities of liquid and vapor phases is important because, water vapor pressure over a solution surface is calculated considering vapor/liquid equilibrium. Equation of states(EOS) of cubic type are used to predict the properties of the mixtures of the refrigerants such as vapor pressure. In these studies various EOS are used such as Redlich-Kwong-Soave equation, Peng-Robinson equation, Patel and Teja equation, and Trebble- Bishnoi equation modified by Salim and Trebble. The parameters in the above equations are based on the experimental data of the partial binary systems [8] and [9]. To find the properties of refrigerant mixture at high pressures (3-4 MPa), the classical models based on a group contribution concept and on excess Gibbs free-energy approach, such as UNIFAC, are not suitable for the scope, as they can be applied successfully only at low pressure. Traditionally, cubic EOS with classical mixing rules are mostly used, and a review of this is given by [10]. In other cases, non-cubic EOS have been proposed, but all of these methods require the knowledge of empirical mixing rules with interaction parameters. These parameters are often of non-predictable nature and a temperature dependent interaction parameter is considered to represent better. But it is shown by [11] that the interaction parameter should also be a composition dependent. Bertucco et al. [9] have used the Redlich-Kwong-Soave EOS to predict the properties of the refrigerant mixtures at low and moderate pressures with the

mixing rules as proposed by Huron and Vidal [12]. The activity coefficient used in the calculation is expressed by a group contribution model derived by UNIFAC.

To estimate the properties of a single desiccant, thermodynamic equilibrium between liquid and vapor has been used in this paper. Various constants such as activity coefficient as given by Robinson [13] and interaction constant as given by Goff et al. [14] are used from the experimental values. In order to estimate the properties of mixture of desiccants, simple mixing rules can be used, unlike the work reported in [9], [8] and [15] who have used mixing rules to find the parameters in the cubic EOS based on experimental data. To estimate the properties of refrigerant mixtures, many equations have been proposed and each year additional ones appear in the literature. But most of them are either totally or at least partially empirical. EOS are based more or less on assumptions which are not generally valid, and at most of the times it becomes difficult to justify mixing rules to express the constants in the equation of the pure components of the mixture as given in [16]. As a result such relationships introduce further arbitrary assumptions. The parameters involved in these equations are based on composition which at most of the times do not involve any arbitrariness. This approach is used in the present analysis to find the thermophysical properties of desiccant mixtures namely calcium chloride and lithium chloride. The same approach can be adopted for any desiccant mixtures.

2.2 Pipeline Drying

The presence of humidity may be detrimental to the operation of pipelines transporting petroleum products. In particular conditions water reacts chemically with hydrocarbons, forming hydrates. Such crystalline substance may cause obstruction of the lines and damage the equipment of the relevant facilities. These drawbacks can be avoided if the water is removed from the line before start-up. The presence of water before starting normal pipeline operation usually results from the hydrostatic testing of the pipelines. Most of the water used for the test can be removed by having sequences of pigs run through the lines. After this operation usually a small amount of water wets the pipe internal wall. This residual water may be eliminated by some drying processes.

Diab [17] used a slug method for drying the gas pipeline with a batch of methanol or glycol for freeze protection and hydrate inhibition. This procedure involves pushing a slug of methanol or glycol through the pipeline between two pigs or spheres. Factors affecting optimization and sizing of the batch are also discussed. Mathematical equations are developed for the optimum concentration and volume of the slug of methanol used to dry the pipeline. It is concluded in the analysis that the lowest slug concentration at the pipe must have a freezing point below the ambient temperature and the final slug concentration must have a concentration high enough to act as a hydrate inhibitor.

Comparing the three spheres method with the two spheres method, the use of three spheres is an improved method to keep the concentration of the methanol in the films left on the pipe wall at a higher level than that of the two spheres method. Improvements such as optimizing the size and concentration of the slug to dry a pipeline by using three spheres method show better results in terms of economy and operation [18].

Battarra et al [19] used dry air method to dry a pipeline. Drying by air can be achieved by having a certain amount of previously dehydrated air run through the pipeline until the concentration of water vapor in the outgoing air reaches a minimum set value. Mathematical methods are used to simulate the process of drying. Partial differential equations for the energy and mass balance are solved numerically with appropriate boundary conditions. Computer code Essic is also developed which allows the fundamental parameters to be optimized. The results obtained by the Essic code proved to be competitive with the methanol swabbing and vacuum drying processes. In addition, this process does not require costly equipment and skilled labour but attains very high drying levels.

Lacasse and Ingvordsen [20] have used solid desiccant to produce dehumidified air to dry gas pipelines. In this study simple equations of specific humidity difference which accounts for only steady state conditions are used. Minimum time required to dry a pipeline is estimated at an inlet air dew point temperature of $-30\ ^{\circ}C$ attained by refrigeration and desiccant dehumidification methods. The proposed system is

simple in operation and less expensive. The mass transfer coefficient between the airstream and water film is not taken into account in the analysis.

Gorislavets and Sverdlov [21] have used a numerical method to dry a pipeline by ventilative drying process. Explicit finite difference scheme with a three levels solution method is used. Results obtained in this study are compared with [19] and a slight difference between these results is observed because Gorislavets and Sverdlov [21] did not considered the change of temperature of the dry air as it flows along the pipeline.

2.3 Regeneration of Liquid Desiccants

Recently attempts have been made to use liquid absorbent in various industrial and solar energy applications. In all these applications an important part of the system is the regenerator, in which the weak absorbent solution is concentrated for reuse. The heat required for the regeneration process can be supplied by any low grade thermal energy. Lof [22] proposed a solar space cooling system in which the room air is dehumidified by hygroscopic triethylene glycol and the dehumidified air is subsequently evaporatively cooled. The weak glycol is regenerated by solar heated air. In such a system the solar heat is first collected at air heating collectors and finally transferred to the absorbent. As a result, the temperature of regeneration is lower than the collector plate temperature and the rate of regenerations is therefore

relatively lower. A typical commercial liquid absorbent dehumidifier/regenerator is shown in Figure 2.1. The strong absorbent is sprayed over the cooling coils in the absorber chamber. Air to be dried passes over the coils in the chamber, where the solution removes moisture from the air. The coolant in the coil removes the heat that is released when the sorbent takes on moisture. The weak solution is then sprayed over a heating coil in the regenerator, the regeneration air picks up the moisture released by the hot solution and exhausting it. The heat for regeneration has traditionally been drawn from fossil fuels. When calcium chloride, lithium chloride, lithium bromide, glycols, etc. are used as the liquid absorbent, effective regeneration may be obtained at temperatures of the order of $50 - 65\ ^{o}C$. These temperatures are also effective operating temperatures for solar collectors. Hence solar energy can be effectively used for such processes. Based on the methods of regenerating the absorbent solutions, regenerators can be divided into different categories as follows:

1. Open - type solar regenerator.

2. Closed - type solar regenerator.

3. Wind forced - flow solar regenerator.

4. Forced - flow solar regenerator.

5. Partly closed - open regenerator.

The merits and demerits of these regenerators can be found in literature. However, in this thesis instead of using thermal energy, a method is proposed to use mechanical energy.

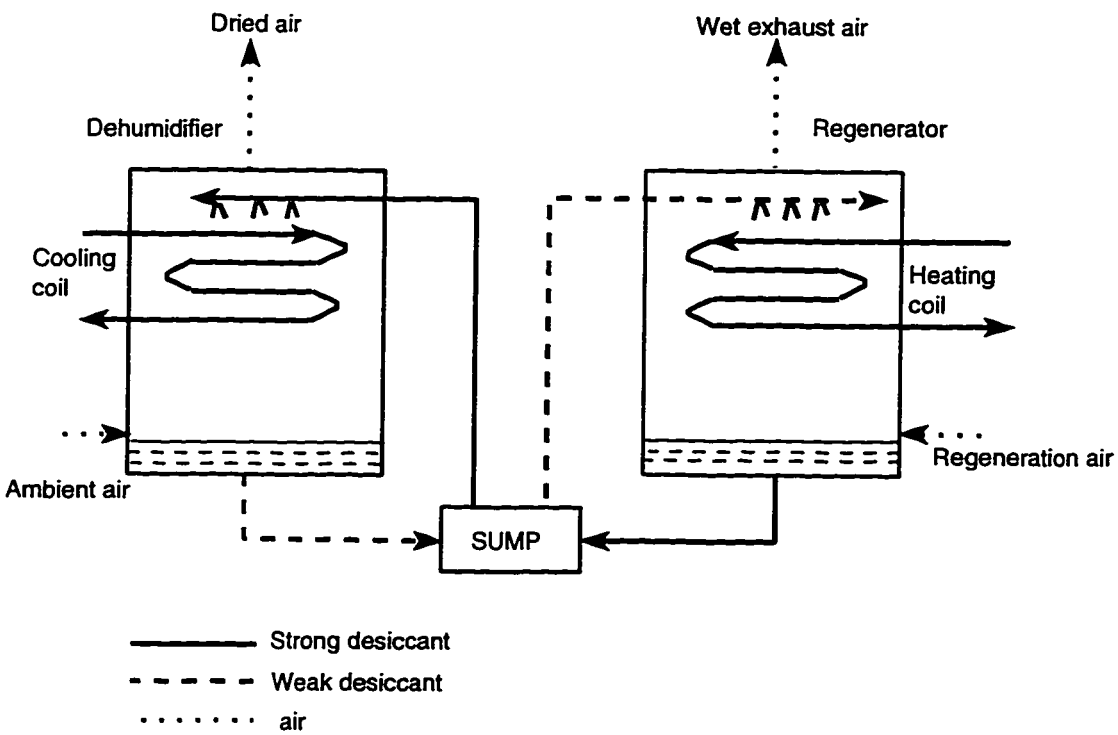

Figure 2.1: Schematic of dehumidifier and regenerator.

Chapter 3

Thermodynamic Analysis of Liquid Desiccants

3.1 Thermodynamics of Vapor - Liquid Equilibrium

One of the characteristics of modern science is abstraction. By describing a difficult, real problem in abstract, mathematical terms, it is sometimes possible to obtain a simple solution to the problem not in terms of immediate physical reality, but in terms of mathematical quantities which are suggested by an abstract description of the real problem. Thermodynamics provides the mathematical language in which an abstract solution of the phase-equilibrium problem is readily obtained [23].

Application of thermodynamics to phase equilibria in multicomponent systems is shown schematically in Fig. 3.1 The real problem is represented by the lower horizontal line. The three-step application of thermodynamics to a real problem consists of defining the problem in abstract terms and solving this problem in terms of abstract quantities and then finally translating the solution back into physical reality. The solution of a phase equilibrium problem using thermodynamics requires three steps: In step 1, the real problem is translated into an abstract mathematical problem; in step 2, a solution is found to the mathematical problem; and in step 3, the mathematical solution is translated back into meaningful terms.

The important feature of step 1 is to define appropriate and useful mathematical functions to facilitate step 2. Chemical potential is such a function. In step 2 a mathematical solution of the problem using thermodynamics is sought simplifying the abstract relation, that is equality of chemical potential to a more meaningful relation, that is equality of fugacity for all the phases at equilibrium.

The step 3 involves translation of the results obtained in step 2 to a meaningful real physical solution.

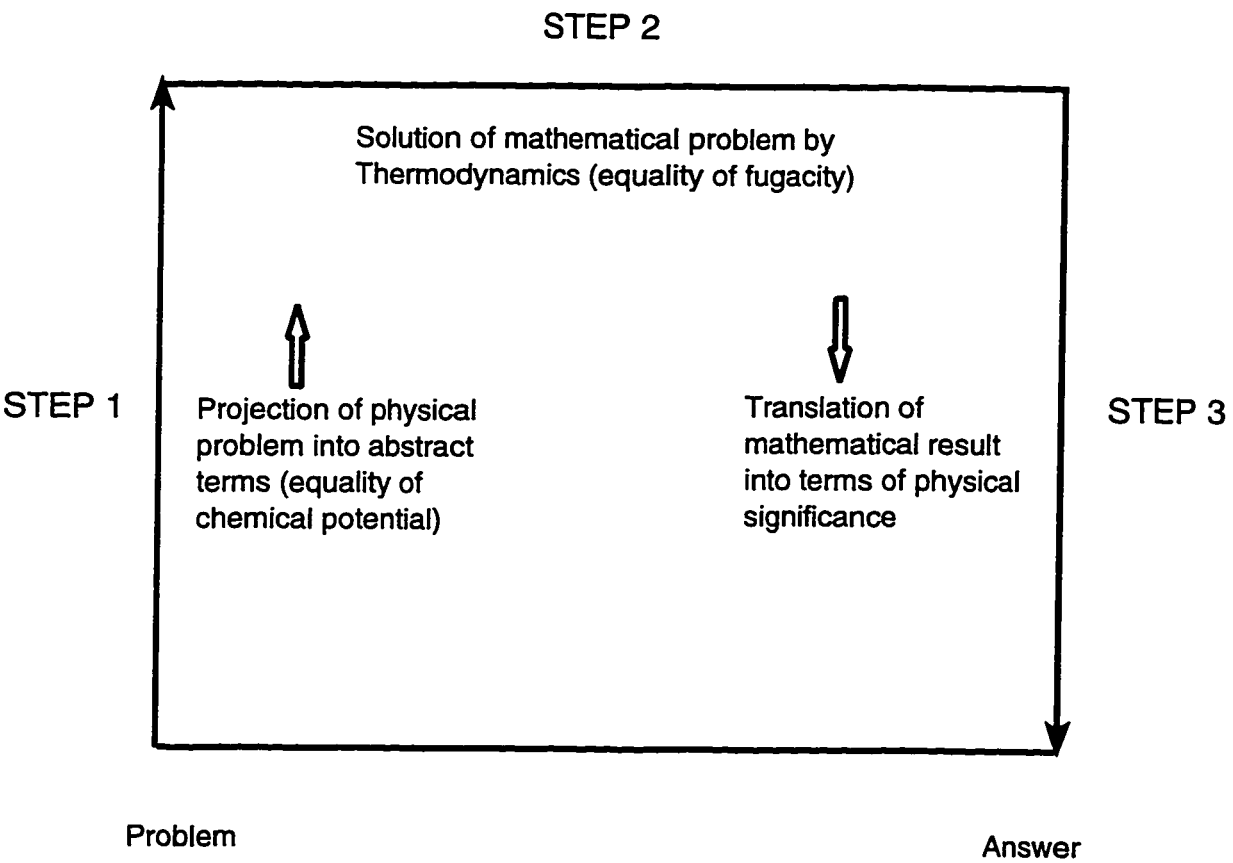

Figure 3.1: Application of thermodynamics to phase - equilibrium problem.

3.2 Chemical Equilibrium

To simplify the analysis initially, consider two phases (α and β), each of which contains 'n' components. These two phases will be considered initially to be in thermal and mechanical equilibrium; that is, they have the same temperature and pressure. Nevertheless, they are not necessarily in phase equilibrium. For systems at constant temperature and pressure one normally apply the general criterion [24]

$$dG_{T,P} \leq 0 \tag{3.1}$$

The change in the Gibbs function for each phase is obtained from,

$$dG = VdP - SdT + \sum_i \mu_i dN_i \tag{3.2}$$

Substituting equation (3.2) in equation (3.1), we get

$$\sum_i \mu_i^\alpha dN_i^\alpha + \sum_i \mu_i^\beta dN_i^\beta \leq 0 \tag{3.3}$$

In addition, in the absence of chemical reactions the moles of each of the i species must be conserved. Thus for the mass transfer process,

$$dN_i^\alpha + dN_i^\beta = 0 \tag{3.4}$$

or

$$dN_i^\alpha = -dN_i^\beta \tag{3.5}$$

The substitution of equation (3.5) into equation (3.3) yields,

$$\sum_i (\mu_i^\alpha - \mu_i^\beta) dN_i^\alpha \leq 0 \tag{3.6}$$

As dN_i^α is nonzero, therefore the above equation yields,

$$\mu_i^\alpha = \mu_i^\beta \tag{3.7}$$

Therefore, the chemical potential of each component is equal at equilibrium.

3.2.1 Equality of Chemical Potential

When the system is in total equilibrium, the chemical potential of any component must be the same. The equality sign in equation (3.6) applies. However, the quantities dN_i^α in the summation are nonzero and independent of each other, therefore, the only way for the left hand side of equation (3.6) is to equal zero, resulting in equation (3.7).

The general result thus obtained is the equality of chemical potential for a system of $'m'$ phases and this can be written as.

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = ...\mu_i^m \tag{3.8}$$

Then the chemical potential of any given component must be same in every phase at phase equilibrium. This is both necessary and mathematically sufficient condition for equilibrium.

3.2.2 Equality of Fugacity

The criterion for phase equilibrium can also be expressed in terms of the fugacities of the components. For a pure component the chemical potential is expressed either in terms of P for an ideal gas or f for a real gas. Consider a mixture of gases. The chemical potential of constituent i in a mixture is based on the pressure or fugacity of the individual component, and it is given as

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \overline{v_i} \tag{3.9}$$

For an ideal gas mixture,

$$V = (N_1 + N_2 + N_3 + N_4 + ...)\frac{RT}{P} \tag{3.10}$$

The partial molar volume of an ideal gas is given as,

$$\overline{v_i} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} = \frac{RT}{P} \tag{3.11}$$

When equation (3.11) is substituted in equation (3.9), we get

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \frac{RT}{P} \tag{3.12}$$

or

$$d\mu_i = RT\ d\ \ln P \tag{3.13}$$

For an ideal gas mixture,

$$p_i = x_i P \tag{3.14}$$

and

$$d\mu_{i,id,T} = RT\ d\ \ln p_i \tag{3.15}$$

Integration of the above equation at constant temperature gives,

$$\mu_{i,id,T} = \mu_{i,ref} + RT \ln \frac{p_i}{p_{i,ref}} \tag{3.16}$$

where $\mu_{i,ref}$ depends on the nature of the gas and the temperature.

Hence, for a real gas in a mixture

$$\mu_i = \mu_{i,ref} + RT \ln \frac{f_i}{f_{i,ref}} \tag{3.17}$$

where f_i is the fugacity of component i in the mixture. The only state where all real gases are truly ideal gases is at zero pressure. This condition is expressed by,

$$lim\ p -> 0 \frac{f_i}{y_i P} = lim\ p -> 0 \frac{f_i}{p_i} = 1 \tag{3.18}$$

where $p_i = y_i P$ and y_i is the mole fraction. Equation (3.17) can also be written as,

$$d\mu_i = RT\ d\ \ln f_i \tag{3.19}$$

Indefinite integration of the above equation gives

$$\mu_i = RT \ln f_i + c \tag{3.20}$$

where c is a constant.

Therefore at phase equilibrium we can state that

$$f_i^1 = f_i^2 = f_i^3 = ...f_i^m \tag{3.21}$$

Thus the fugacity of a given component must be the same in each phase. This criterion is more useful than that of the chemical potential [25].

3.2.3 Vapor-Liquid Equilibrium

Consider the equilibrium distribution of a component in a binary system of vapor and liquid phases. By the assumption of ideal behavior, for any component i, the equilibrium equation says that,

$$f_i^v = f_i^l \tag{3.22}$$

where the fugacity of component i in the vapor phase at constant temperature and pressure is given by

$$f_i^v = y_i f_{i,pure}^v \tag{3.23}$$

The fugacity of pure i in a vapor is given by

$$f_{i,pure}^v = \varphi_i P \tag{3.24}$$

Combining the above two equations

$$f_i^v = y_i \varphi_i P \tag{3.25}$$

where φ_i indicates the departure from ideal behavior.

Similarly the fugacity of component i in the liquid phase is given by,

$$f_i^l = x_i \gamma_i \varphi_i^{sat} P_i^{sat} \tag{3.26}$$

Therefore, for equilibrium between vapor and liquid is given by combining the above equations (3.25) and (3.26).

$$y_i \varphi_i P = x_i \gamma_i \varphi_i^{sat} P_i^{sat} \tag{3.27}$$

The mole fraction or the vapor pressure of the component i, can be determined using the above equation.

3.3 Determination of Fugacity coefficients

Equation (3.27) can be used to find the mole fraction in the liquid phase or the vapor pressure of water vapor over the solution surface at equilibrium. The terms φ_i and φ_i^{sat} can be determined using temperature and volume as independent variables, using Helmholtz free energy function [23].

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j} \tag{3.28}$$

where F is the Helmholtz free energy of the mixture.

$$F = U - TS \tag{3.29}$$

where U is the internal energy of the mixture. Both U and S can be expressed in terms of T and V as follows:

$$U = \int_V^\infty \left[P - T\left(\frac{\partial P}{\partial T}\right)_{V,N}\right] dV + \sum_i n_i u_i^o \tag{3.30}$$

where u_i^o is the molar internal energy of pure i as an ideal gas at temperature T, and

$$S = \int_V^\infty \left(\frac{NR}{V} - \left(\frac{\partial P}{\partial T} \right)_{V,N} \right) dV + R \sum_i n_i \ln \left(\frac{V}{n_i RT} \right) + \sum_i n_i s_i^o \qquad (3.31)$$

Hence,

$$F = \int_V^\infty \left(P - \frac{NRT}{V} \right) dV - RT \sum_i n_i \ln \left(\frac{V}{n_i RT} \right) + \sum_i n_i \left(u_i^o - T s_i^o \right) \qquad (3.32)$$

and taking

$$\mu_i^o = u_i^o - T s_i^o, \qquad (3.33)$$

$$\mu_i = \left(\frac{\partial F}{\partial n_i} \right)_{T,V,n_j} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln \left(\frac{V}{n_i RT} \right) + \mu_i^o \qquad (3.34)$$

Again, with the convention $f_i^o = 1\ atm$ and substracting RT ln $(y_i P)$on both sides of the above equation, we get:

$$RT \ln \left(\frac{f_i}{y_i P} \right) = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z \qquad (3.35)$$

where z is the compressibility factor and is given by

$$z = \frac{PV}{NRT} \qquad (3.36)$$

The problem is now to find the volume $V$of the mixture in terms of P, T and n_i or the pressure in terms of V, T and n_i. If P is not too high, the virial equation of state for the mixture can be used.

The virial equation of state gives z as a power series in terms of $v = \frac{V}{N}$,

$$z = 1 + \frac{B}{v} + \frac{C}{v^2} + ... \tag{3.37}$$

where B, termed the second virial coefficient, takes into account deviations from ideal behavior which result from collisions or interactions that involve two molecules at a time. The third virial coefficient, C, takes into account deviations due to interactions of three molecules at a time and so on for higher order coefficients.

In terms of P, the virial equation becomes:

$$z = 1 + \frac{B}{RT}P + \frac{C - B^2}{(RT)^2}P^2 + ... \tag{3.38}$$

For a mixture of n components,

$$B_{mix} = \sum_{i=1}^{n}\sum_{j=1}^{n} y_i y_j B_{ij} \tag{3.39}$$

where B_{ii} is the second virial coefficient of pure i and $B_{ij}, i \neq j$ is the interaction constant between components i and j .

For a binary mixture, this equation reduces to:

$$B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \tag{3.40}$$

Similarly interaction between three molecules i, j and k,

$$C_{mix} = \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} y_i y_j y_k C_{ijk} \tag{3.41}$$

Using Equation (3.35),

$$RT \ln \varphi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_J} - \frac{RT}{V} \right] dV - RT \ln z \tag{3.42}$$

and the virial equation for a mixture is given by,

$$z_{mix} = \frac{Pv}{RT} = 1 + \frac{B_{mix}}{v} + \frac{C_{mix}}{v^2} + ... \tag{3.43}$$

The fugacity coefficient for any component i in a mixture of n components is obtained by substitution in equation (3.42). When the indicated differentiation and integration are performed, we obtain

$$\ln \varphi_i = \frac{2}{v}\sum_{j=1}^{n} y_j B_{ij} + \frac{3}{2v^2}\sum_{j=1}^{n}\sum_{k=1}^{n} y_j y_k C_{ijk} - \ln z_{mix} \tag{3.44}$$

The third virial coefficient C_{ijk} are scarcely available even for pure substances, therefore they are usually neglected. This is a good approximation as long as the pressure remains low.

In the same way φ_i^{sat} can be determined using

$$\ln \varphi_i^{sat} = \frac{B_{ii} P_i^{sat}}{RT} \tag{3.45}$$

φ_i^{sat} can then be used in equation (3.31) for calculating the mole fraction or the vapor pressure of component i.

3.4 Thermodynamics of Liquid Desiccant Solutions

In applying the concept of equilibrium to liquid desiccant system, we have to consider three components namely air , water, and the liquid desiccant.

Let air be component 1.

Water be component 2.

Liquid desiccant be component 3.

Assume that the air is not dissolved in the liquid mixture and therefore,

$$x_1 \cong 0 \tag{3.46}$$

Liquid desiccant usually has very small saturation pressure, and hence

$$y_3 \cong 0 \tag{3.47}$$

Water is present both as vapor and liquid, therefore the equilibrium applies:

$$y_2\varphi_2 P = x_2\gamma_2\varphi_2^{sat}P_2^{sat} \tag{3.48}$$

One has to satisfy the following two conservation equations.

$$y_1 + y_2 = 1 \tag{3.49}$$

and

$$x_2 + x_3 = 1 \tag{3.50}$$

To calculate the mole fraction or the vapor pressure of water over the solution, one has to determine φ_1 ,φ_2^{sat} and γ_2.

γ_2 can be taken from [13].

In order to determine φ_1 and φ_2^{sat}, we need the virial equation of state of humid air. It is given by,

$$z_{ha} = 1 + \frac{B_{ha}}{v} + ... \tag{3.51}$$

where

$$B_{ha} = y_1^2 B_{11} + 2y_1y_2B_{12} + y_2^2B_{22} \tag{3.52}$$

The virial equation second coefficient of air B_{11} is given by Beattie and Stockmayer [26],

$$B_{11} = A_o - \frac{B_o}{RT} - \frac{C_o}{RT^2} \quad in\ liters/mole \tag{3.53}$$

where

$$\begin{aligned} A_o &= 0.04611 \\ B_o &= 1.3012 \\ C_o &= 4.34 * 10^4 \\ R &= 0.08206 \end{aligned}$$

B_{12} in $cm^3/mole$ is given by Goff et al. [14] as a function of T as:

$$B_{12} = \frac{16274}{T} 10^{\frac{43}{T}} - 4.25 \tag{3.54}$$

The interaction constant between the component 1 and 2 is given as

$$\zeta_{12} = \frac{2B_{12}}{B_{22} + B_{11}} \tag{3.55}$$

Therefore, B_{22} used in equation (3.52) can be determined using the above equation.

Chapter 4

Desiccant Mixtures

4.1 Introduction to Mixtures

Experiments have been done with desiccant solutions of two or more salts in an effort to find a combination which would produce maximum depression in the properties [27]. Generally speaking, such desiccants show lower water vapor pressure than those of either of the two desiccant solutions at any given temperature ordinarily encountered in air dehumidification. By combining different liquid desiccants improved characteristics can be expected as well as a considerable reduction in cost. Some available desiccants have high costs and some other possess poor properties. To stabilize these desiccants and to lower the high cost, and to improve the properties of the desiccants, they can be mixed in different combinations. In most of the applications the general properties that are required are low vapor pressure,

high elevation of boiling point, high latent heat of condensation and dilution heat, low crystallization point for the easy handling at low temperature, and low cost. These requirements are not fully answered by any single desiccant, but after making some compromises liquid desiccants can be mixed in different proportions to obtain mixtures with improved properties and of low cost.

4.1.1 Mixing Rules

There are general mixing rules or equations for each class of mixtures and one must select the proper type of equation for accurate estimation of any given property. One must also know what information is required in addition to the corresponding property of the components and their concentrations in order to make valid estimates of the properties of the mixture.

It would be desirable to be able to predict easily the properties of the mixtures from just the corresponding properties of the components and their concentrations. However, in general additional information must be known about the nature of the mixture if accurate prediction of properties is to be made. These information includes interactions between the constituents, particle size and shape, and nature of the packing found in the mixture. Many equations of both theoretical and empirical nature can be found in the literature for predicting the properties of the mixture [16]. Many of these equations can be shown derivable from only a few simple, but very general mixing rules. The simplest mixture rule is often called, the rule of

mixture, it is given as,

$$E = E_a\psi_a + E_b\psi_b \tag{4.1}$$

The concentration terms may be either weight fraction or volume fraction depending upon the kind of property being measured. Another equation which also predicts the properties of the mixture with good accuracy is the inverse rule of mixtures, and is given as,

$$\frac{1}{E} = \frac{\psi_a}{E_a} + \frac{\psi_b}{E_b} \tag{4.2}$$

The above two equations require that one only needs to know the value of the given property for each component and their concentration. The concentrations are related as,

$$\psi_a + \psi_b = 1.0 \tag{4.3}$$

4.1.2 Interaction Parameter

In the great majority of mixtures the simplest mixture rules are not capable of accurately predicting the properties of a binary mixture. To make accurate predictions some kind of additional information must be supplied to an equation appropriate to the type of the mixture. For one phase system,

$$E = E_a\psi_a + E_b\psi_b + I\psi_a\psi_b \tag{4.4}$$

where I is the Interaction parameter which can be either positive or negative depending on the system, and this is a new factor in a mixture which did not exist in the pure components. These parameters are often of non-predictable nature. However, in most of the cases these are temperature as well as concentration dependent [16]. In the present analysis, interaction parameter is determined by taking the product of the concentration of the individual components.

4.2 New Liquid Desiccant Mixture

Desiccants or absorbents are the materials that has a tendency to absorb moisture when humid air is brought into contact with them. Several experiments have been carried out by mixing two or more desiccants in different proportions [6] and [7], and the results obtained from these experiments show that the resulting new desiccant will possess better operating characteristics than a single desiccant and in addition it is cost effective. In the present study, simple mixing rules with and without interaction parameter are used to determine the thermophysical properties, such as vapor pressure, density and viscosity of the desiccant mixtures. Desiccants studied in the analysis are lithium chloride and calcium chloride. Values computed here are compared with the only available experimental results for these properties.

4.3 Thermophysical Properties

The sorbent solution thermophysical properties required by many thermal system are vapor pressure, solubility, viscosity, density, specific heat, and thermal conductivity. Among these properties, the only properties for the mixture of lithium chloride and calcium chloride at 50% concentration of each with $20\% - 30\%$ overall concentration available in the literature are vapor pressure, density and viscosity. Therefore, the same properties are estimated using the simple mixing rules with and without interaction parameter.

Vapor pressure of a solution is the pressure of the vapor that is in equilibrium with the solution at a given temperature. By using the data for lithium chloride and calcium chloride from Uemura [28] and Dow chemical [29] respectively, the vapor pressure of the mixture of lithium chloride and calcium chloride is determined for different concentrations using the simple mixing rules. Values are estimated at 20%, 30% and 40% overall concentration with 50% concentration of each component. These values are computed with and without interaction parameter as given in equations(4.1) and (4.4) respectively. Similarly the two other important properties, density and viscosity are also determined. Density is important for the analysis of any thermal system utilising desiccant. Viscosity is important in determining the pumping power required to pump the desiccant. Both density and viscosity of the mixture of lithium chloride and calcium chloride are determined at 30, 35 and 40%

overall concentration with 50% concentration of each desiccant.

Chapter 5

Drying of Pipeline

5.1 Importance of Pipeline Drying

Prevention of hydrates buildup and corrosion in gas pipelines after hydrostatic testing is increasingly important to those in the gas industry.

Hydrostatic tests are performed prior to commissioning the new pipelines. Residual water can remain on the pipe wall as a thin moisture film typically 0.1 to 0.15 mm thick. If allowed to remain in the pipeline, this free water can react with hydrocarbon gases to form hydrates which form on the internal pipe wall, thus causing increasing friction and causing loss of pipeline efficiency.

Many methods have been tried to ensure that no residual moisture remains in the pipelines. Some methods include the use of nitrogen, methanol, natural gas, and vacuum. However, because of economics, technical feasibility, and safety, many

of these methods have proved to be less than satisfactory. The dry air method is considered to be cost effective as well as environmental friendly. In this method atmospheric air is dried to a low dew point, thus providing a low vapor pressure to the dry air as it is introduced in the pipeline. This low vapor pressure air provides the driving force for drying the pipeline.

5.2 Psychrometric of Dehumidification

The principle in the dry air method of drying pipelines consists of blowing a low dew point air into the pipeline. Moisture will be absorbed in the dry airstream since low dew point air has a low vapor pressure. This vapor pressure difference between the moisture content in the pipeline and the dry air moisture content is the driving force for drying. Greater the difference, faster the pipeline will be dried. To obtain low dew point air, it is necessary to use both the mechanical refrigeration and the desiccant dehumidification process as shown in Fig. 5.1. The process consists of two stages and the psychrometric of drying process is shown in Fig. 5.2.

The first stage of the dehumidification process uses mechanical refrigeration to chill the air below its dew point. Air is first passed through the cooling coil, where it is sensibly cooled from state 1 to 2 as shown in Fig. 5.2 and the moisture is then removed by condensation from state 2 to 3. Usually air is cooled to approximately 4 ^{o}C. Below this temperature, condensed moisture would freeze on the cooling coil

stopping the dehumidification process. Hence, the second stage of dehumidification is accomplished by using a liquid desiccant dehumidifier as shown in the Fig. 5.1. In the dehumidifier air is made to pass through a spray of liquid desiccant which is sprinkled from the top of the dehumidifier. The desiccant is efficient at removing moisture and thus makes the air to reach a final dewpoint of $-20\ ^{o}C$ to $-40\ ^{o}C$. This process is shown as state 3 to 4 on the psychrometric plot. Therefore, the desiccant dehumidifier can work at any temperature without freezing up.

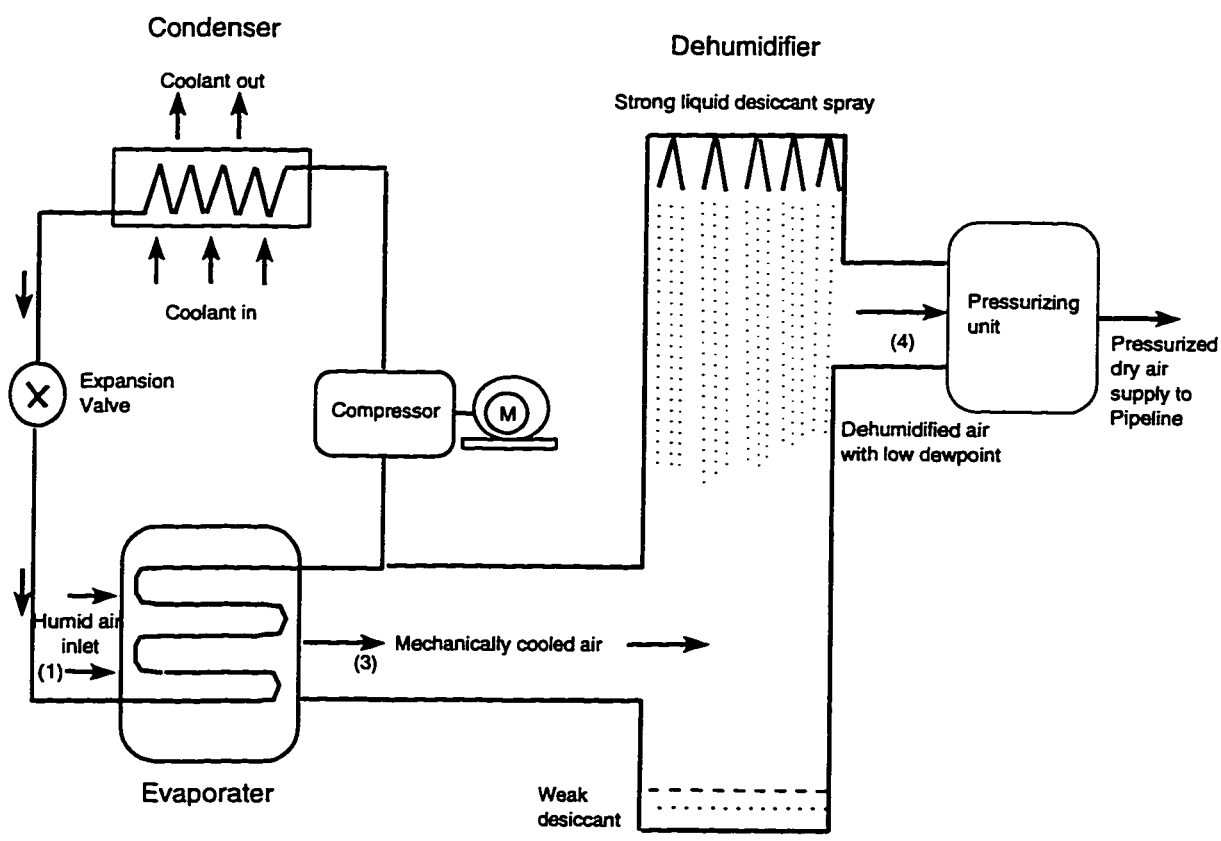

Figure 5.1: Schematic of pipeline drying process.

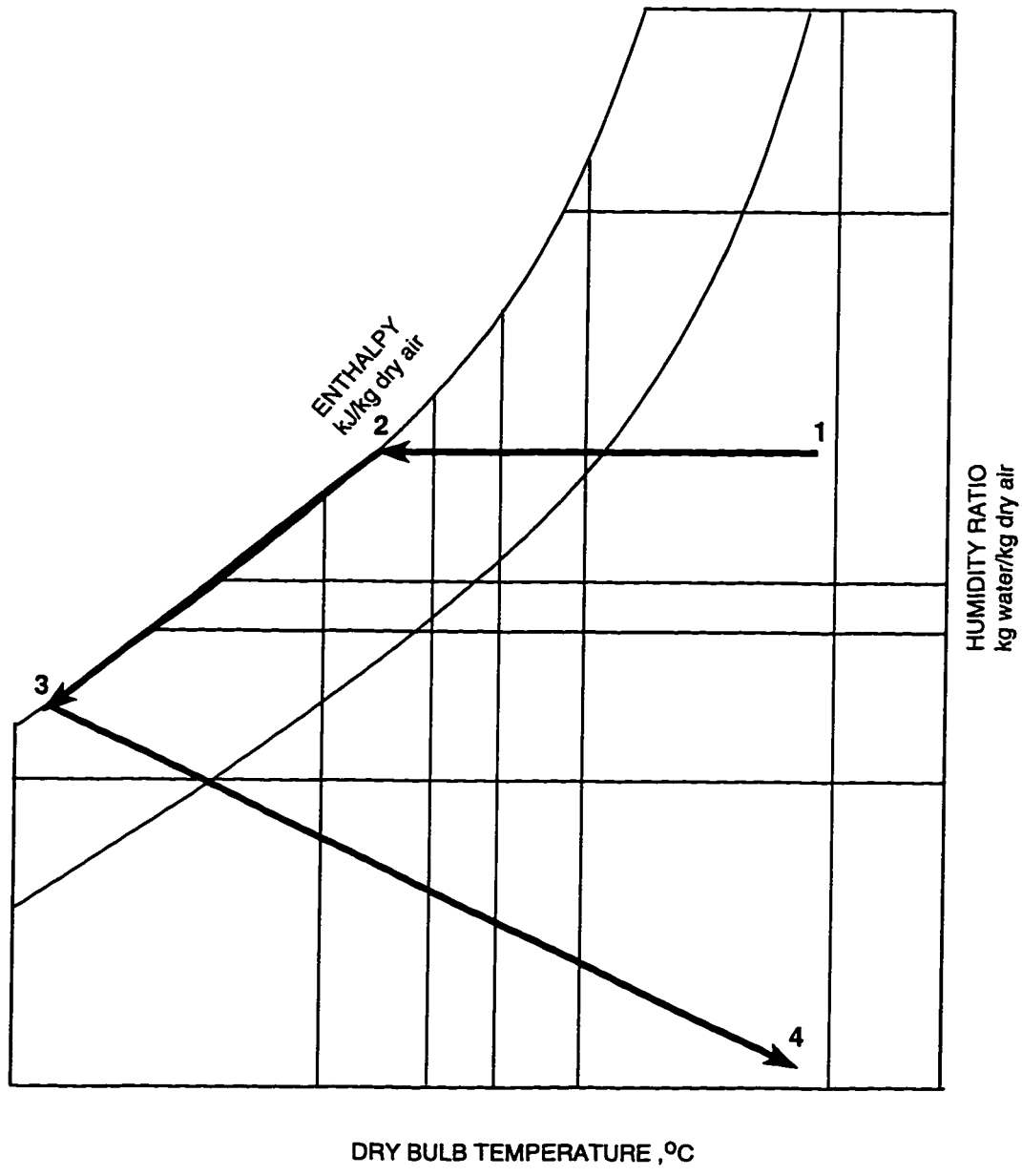

Figure 5.2: Psychrometric of drying process.

5.3 Mathematical Modelling

One of the most important aspects of drying technology, especially for industrial processes, is mathematical modelling of the drying processes. The purpose of modelling is to allow the engineer to choose the most appropriate method of drying a given product as well as to choose suitable operating conditions.

The principle of modelling is based on having a system of mathematical equations which completely characterize the system to be modelled. In particular the solution of these equations makes it possible to predict the parameters of the process as a function of time at any point based on given initial and boundary conditions.

The drying process by using the dehumidified air is schematized as shown in Fig. 5.3 by making some simplifications that are justified by the fact that the vapor mass concentration in the flowing air - vapor mixture remains very low. In particular, the following assumptions are made:

1. The dry air behaves like an ideal gas, that is we can assume that the gas containing the moisture obeys all the laws of ideal gases.

2. The pressure profile along the pipeline can be calculated as for the same air flow rate in a single-phase steady flow without evaporation.

3. Influence of the temperature drop of the air due to the moisture evaporation from the pipe wall on the drying time is neglected.

4. Wall temperature is assumed to be equal to the ambient temperature.

5. Initially the whole system is assumed to be at a temperature equal to the atmospheric temperature.

6. Film thickness on the pipeline wall is assumed to be constant.

7. All the terms for kinetic energy and the action of gravity are neglected.

The mass conservation on the element Δx shown in the Figure 5.3 can be written as,

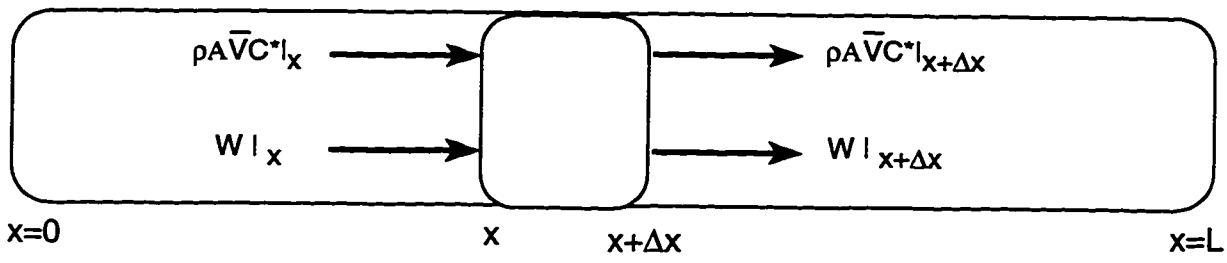

Figure 5.3: Schematic of a pipeline.

$$Accumulation = Input - output + generation - destruction$$

As there is no generation or the destruction term in the drying process, the above equation reduces with the first two terms,

$$\frac{\partial W}{\partial t} = -\pi D N_A \tag{5.1}$$

and

$$\frac{\partial}{\partial t}(\rho A \Delta x C^*) = \rho A \overline{V} C_x^* + \pi D \Delta x N_A - \rho A \overline{V} C_{x+\Delta x}^* \tag{5.2}$$

After simplification,

$$\rho A \frac{\partial C^*}{\partial t} = -Q \frac{\partial C^*}{\partial x} + \pi D N_A \tag{5.3}$$

where $Q = \rho A\overline{V}$

The above equations (5.1) and (5.3) express the mass conservation of water respectively, in the liquid and vapor phases, and they can be solved analytically as well as numerically with the following initial and boundary conditions:

$$W(x,0) = W_o \tag{5.4}$$

$$C^*(x,0) = C^*_{sat} \tag{5.5}$$

$$C^*(0,t) = C^*_o \tag{5.6}$$

$$\frac{\partial C^*}{\partial x}(L,t) = 0 \tag{5.7}$$

The expression describing the rate of mass transfer in the saturated section for a binary gaseous system with one diffusing component is given [30] as,

$$N_A = \frac{N_A}{N_A + N_B} F \ln \left(\frac{\frac{N_A}{N_A+N_B} - C_{A2}/C}{\frac{N_A}{N_A+N_B} - C_{A1}/C} \right) \tag{5.8}$$

where C_A/C is the mole fraction concentration with C_{A2}/C and C_{A1}/C representing in the stream core and saturation at pipe wall respectively.

$C_A/C = X_A$ for liquids

and $C_A/C = Y_A$ for gases.

In the present analysis we consider only the transfer of liquid component A from the water film on the pipe wall to the dry gas given by component B.

Therefore,

$$\frac{N_A}{N_A + N_B} = 1 \tag{5.9}$$

Since $N_B = 0$,

the above equation (5.8) reduces to

$$N_A = F \ln \left(\frac{1 - C_{A2}/C}{1 - C_{A1}/C} \right) \tag{5.10}$$

By analogy with equation (5.10), the mass flux of water vapor in the saturated section can be found from the equation given below:

$$N_A = F \ln \left(\frac{1 - Y}{1 - Y_{sat}} \right) \tag{5.11}$$

The molar content of moisture at the pipe wall is determined in turn, as the limiting content expressed in molar fraction [30]. It can be given as,

$$Y_s = \frac{P_{sat}}{P - P_{sat}} \tag{5.12}$$

The mass transfer coefficient F is determined from the expression given in [31],

$$F = \frac{0.023 MW_v D_{va} \rho}{MW_a D} \left(\frac{\nu}{D_{va}} \right)^z Re^{0.8} \tag{5.13}$$

The exponent z in equation (5.13) depends on Reynolds number. As the flow is assumed to be turbulent therefore, for $Re > 10^4$, it can be taken as unity.

Therefore, equation (5.13) reduces to

$$F = \frac{0.023 MW_v \eta}{MW_a D} Re^{0.8} \tag{5.14}$$

In order to use equation (5.11) one has to determine the molar fraction Y of water vapor in the stream core. This can be determined in terms of the mass fraction C^* of water vapor by solving equations (5.1) and (5.3) along with initial and boundary conditions.

5.4 Analytical Method for Determining the Variation of Concentration

In order to determine the variation of concentration of water vapor in the dry air, a linear functional form for N_A is suggested as given below, because the transform cannot be used due to the presence of non-linearity in N_A.

Equation representing the mass conservation of water in the liquid and vapor phase is solved analytically using the Laplace transforms for the variation of concentration of the water vapor in the drying air, and for predicting the drying time required to dry a pipeline of given length for different operating parameters.

The rate of mass transfer term N_A can be assumed as a linear function as,

$$N_A = a_1 + b_1 C^* \tag{5.15}$$

where a_1 and b_1 are constants and can be determined using the equation given below:

$$N_A = \beta_1 (P_{sat} - P_\infty) \tag{5.16}$$

where

$$\beta_1 = \frac{0.622k}{P}\, kg/hm^2\,(mmHg) \tag{5.17}$$

and

$$\frac{h}{k} = 950\, J/kgK \tag{5.18}$$

Equation (5.3) can be rewritten as,

$$\frac{\partial C^*}{\partial t} = -\frac{Q}{\rho A}\frac{\partial C^*}{\partial x} + \frac{\pi D N_A}{\rho A} \tag{5.19}$$

By substituting the value of N_A in equation (5.19), it reduces to,

$$\frac{\partial C^*}{\partial t} = -\delta\frac{\partial C^*}{\partial x} + \omega\,(a_1 + b_1 C^*) \tag{5.20}$$

where

$$\delta = \frac{Q}{\rho A} \tag{5.21}$$

and

$$\omega = \frac{\pi D}{\rho A} \tag{5.22}$$

Applying Laplace Transform to equation (5.19),

$$\mathrm{L}\left(\frac{\partial C^*}{\partial t}\right) = -\delta \frac{\partial C^*}{\partial x} + \omega \mathrm{L}\left(a_1 + b_1 C^*\right) \tag{5.23}$$

Taking Laplace Transform on the transient term of equation (5.23),

$$\mathrm{L}\left(\frac{\partial C^*}{\partial t}\right) = SC^*(x,s) - C^*(x,0) \tag{5.24}$$

Substituting equation (5.24) in equation (5.23), we get,

$$SC^*(x,s) - C^*_{sat} = -\delta \frac{\partial C^*}{\partial x} + \omega \left[\left(\frac{a_1}{s}\right) + b_1 C^*\right] \tag{5.25}$$

The above equation can be simplified as,

$$\left[\delta \frac{d}{dx} + (s - b_1\omega)\right] C^* = \left(C^*_{sat} + \frac{\omega a_1}{s}\right) \tag{5.26}$$

The solution of this equation is [32],

$$c = c_p + c_c \tag{5.27}$$

where

$$c_c = A_1 \exp\left[-\left(\frac{s - b_1\omega}{\delta}\right)x\right] \tag{5.28}$$

c_p can be calculated as,

$$c_p = \int_{u=0}^{x} \left(\frac{\omega a_1}{\delta s} + \frac{C^*_{sat}}{\delta}\right) \exp\left[-\left(\frac{\omega b_1 - s}{\delta}\right)(U1 - x)\right] dU1 \tag{5.29}$$

Solving the above equations and substituting the value of c_c and c_p in equation (5.27), we get,

$$C^* = C^*_{sat} e^{\omega b_1 x/\delta} + \frac{a_1}{b_1}\left(e^{\omega b_1 t} - 1\right) + C^*_{sat} e^{\omega b_1 t} - \left[\frac{a_1}{b_1}\left(e^{\omega b_1 (t - x/\delta)} - 1\right) + C^*_{sat} e^{\omega b_1 (t - x/\delta)}\right] e^{\omega b_1 x/\delta} \tag{5.30}$$

The variation of concentration of water vapor in the dry air can be determined for different x and t by using the above equation.

5.5 Numerical Method

The numerical solution for the system of equations (5.1) and (5.3) is also carried out using semi-implicit finite difference scheme. In this scheme, the equation is juxtaposed in two difference equations as given below:

$$\frac{\partial C^*}{\partial t} = \frac{Q}{A\rho}\frac{\partial C^*}{\partial x} \tag{5.31}$$

and

$$\frac{\partial C^*}{\partial t} = \frac{Q}{A\rho}\frac{\partial C^*}{\partial x} + \frac{\pi D N_A}{A\rho} \tag{5.32}$$

In the equation (5.31) the value of C^* is determined at an intermediate time level without involving the nonlinear term in N_A.

In equation (5.32) value of C^* is determined at the next time level, in this way the solution marches in the forward direction.

The complete non-dimensionalization and the discretization of the equations (5.1) and (5.3) are as follows:

Let us take the following non-dimensional parameters,

$$\phi = \frac{C^*}{C^*_{sat}} \tag{5.33}$$

$$\varphi = \frac{\overline{V}}{\overline{V}_o} \tag{5.34}$$

$$\eta = \frac{x}{L} \tag{5.35}$$

$$\psi = \frac{N_A}{N_{Ao}} \tag{5.36}$$

$$\tau = \frac{t}{t_o} \tag{5.37}$$

$$\Psi = \frac{W}{W_o} \tag{5.38}$$

After non-dimensionalization equations (5.1) and (5.3) reduces to,

$$\frac{\partial \phi}{\partial t} = -\alpha_1 \left[\frac{3}{4}\phi + (\frac{3}{4}\eta + \frac{1}{4})\frac{\partial \phi}{\partial \eta}\right] + \beta_1 \left[1 + 237.6 \ln(1 - .0323\phi)\right] \tag{5.39}$$

and

$$\frac{\partial \Psi}{\partial t} = -\sigma\psi \tag{5.40}$$

The equations (5.31) and (5.32) after non - dimensionalization reduces to,

$$\frac{\partial \phi}{\partial t} = -\alpha_1 \left[\frac{3}{4}\phi + (\frac{3}{4}\eta + \frac{1}{4})\frac{\partial \phi}{\partial \eta}\right] \tag{5.41}$$

and

$$\frac{\partial \phi}{\partial t} = -\alpha_1 \left[\frac{3}{4}\phi + (\frac{3}{4}\eta + \frac{1}{4})\frac{\partial \phi}{\partial \eta}\right] + \beta_1 \left[1 + 237.6 \ln(1 - .0323\phi)\right] \tag{5.42}$$

The discretization of equations (5.41) and (5.42) is done by considering a three time level solution method, with ϕ_i^n, $\overline{\phi}_i^{n+1}$ and ϕ_i^{n+1} representing the values at first, intermediate and final time level respectively.

$$\frac{\overline{\phi}_i^{n+1} - \phi_i^n}{\Delta t} = -\alpha_1 \left[\frac{3}{4}\phi_i^n + \left(\frac{3}{4} i * h + \frac{1}{4}\right)\left(\frac{\phi_{i+1}^n - \phi_{i-1}^n}{2h}\right)\right] = 0 \tag{5.43}$$

Discretization of equation (5.41) results as,

$$\overline{\phi}_i^{n+1} = -\Delta t * \alpha_1 \left[\frac{3}{4}\phi_i^n + \left(\frac{3}{4}i * h + \frac{1}{4}\right)\left(\frac{\phi_{i+1}^n - \phi_{i-1}^n}{2h}\right)\right] + \phi_i^n \tag{5.44}$$

Equation (5.42) can be discretized as,

$$\frac{\phi_i^{n+1} - \phi_i^n}{\Delta t} = -\alpha_1 \left[\frac{3}{4}\overline{\phi}_i^{n+1} + \left(\frac{3}{4}i * h + \frac{1}{4}\right)\left(\frac{\overline{\phi}_{i+1}^{n+1} - \overline{\phi}_{i-1}^{n+1}}{2h}\right)\right] + \beta_1 \left[1 + 237.6 \ln(1 - .0323\phi_i^n)\right] \tag{5.45}$$

On simplifying the above equation reduces to,

$$\phi_i^{n+1} = -\Delta t * \alpha_1 \left[\frac{3}{4}\overline{\phi}_i^{n+1} + \left(\frac{3}{4}i * h + \frac{1}{4}\right)\left(\frac{\overline{\phi}_{i+1}^{n+1} - \overline{\phi}_{i-1}^{n+1}}{2h}\right)\right] + \Delta t * \beta_1 \left[1 + 237.6 \ln(1 - .0323\phi_i^n)\right] + o_i^n \tag{5.46}$$

and

$$\frac{\Psi_i^{n+1} - \Psi_i^n}{\Delta t} = -\sigma\psi \tag{5.47}$$

The set of equations (5.44), (5.46) and (5.47) are solved numerically with the boundary and initial conditions.

In the numerical solution of problems of the fluid flow, the steps of the difference grid are chosen in accordance with the necessary conditions of stability, which are found by the conditional setting of certain unknown functions of the system. Systems

in which the thermophysical properties are assumed to be constant, dry air behaves like an ideal gas and the spatial steps are equal in all directions.

By satisfying the conditions of stability the time difference step is defined as,

$$m = \frac{h}{u} \tag{5.48}$$

Depending on the above stability critiria, the spatial step, h is selected.

Chapter 6

Regeneration

6.1 Regeneration of Liquid Desiccants

Recently attempts have been made to use liquid desiccants in various drying and dehumidifying applications. In all these applications an important part of the system is the regenerator, in which the weak desiccant is reconcentrated. The heat required for the regeneration of the weak desiccant solution can be supplied by fossil fuel, solar energy, waste heat or any form of low grade thermal energy. Most of these processes are either costly or a function of climatic conditions. In the present study an attempt is made to use mechanical energy for regeneration. Reverse Osmosis has been used for desalination of sea water in which saline water with some concentration of dissolved salts is concentrated to pure water when passed through membrane, thereby concentrating the saline water to a higher degree. In a similar manner,

weak desiccant can be concentrated by removing the water from the solution.

6.2 Osmosis Process

Osmosis is a process in which the solvent is transported through the membrane as a result of a difference in trans-membrane concentration as shown in Figure 6.1.

If the system is not subjected to any external influence such as removal of excess of solvent results in the establishment of hydrostatic pressure difference. At this point the net material transport has reached zero. This condition is known as osmotic equilibrium, and the corresponding pressure difference is referred to as osmotic pressure. Osmotic equilibrium is a hydrodynamic equilibrium, solvent still passes through the membrane but fluxes are statistically the same in both directions.

6.3 Reverse Osmosis Process

The reverse osmosis process is characterized by the use of pressure in excess of osmotic pressure to force the solution of salt at ambient temperature through a selective membrane capable of rejecting the dissolved salts. The process name is derived from the phenomenon whereby the water under an applied pressure driving force flows in the opposite direction to that normally observed in an osmotic process where the driving force is the concentration gradient.

If the trans-membrane pressure difference greater than that of corresponding to

osmotic equilibrium is applied to the test cell, then the solvent flux can be reversed and the solution with the greater concentration is further concentrated . This flux reversal is the reason for the rather unfortunate name reverse osmosis (RO), in principle, RO, i.e, a membrane process with a high trans-membrane pressure difference may also be used for separating organics or aqueous-organic mixtures.

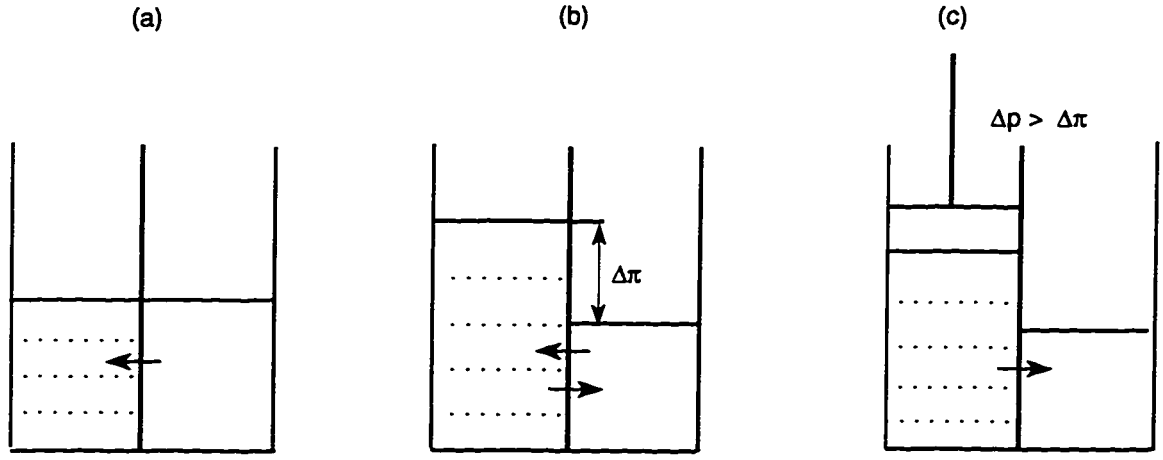

Figure 6.1: Osmosis and Reverse Osmosis: (a) Osmosis (b) Osmotic equilibrium (c) Reverse osmosis, $\Delta p > \Delta \pi$

6.4 Membranes

Membranes research is intricately linked with the final application. This point is of particular relevance for ion-selective membranes, and applies to gas permeation and pervaporation to a lesser extent.

Membrane processes involve different processes and hence it might be expected that a number of very different membranes are necessary. This is especially so because even for a single process such as reverse osmosis, one type of membrane is not sufficient to cover all possible applications of reverse osmosis. Membrane processes would never have achieved such a high industrial status, however, if one membrane had not been able to solve more than just one problem [33].

Composite membranes produced for sea water desalination, for example, have also been used successfully for treating process and effluent water containing components such as acetic acid, ethylene glycol, phenols or pigments. Cellulose acetate provides a further example, being used extensively, with slight modifications, for a wide range of problems in the fields of reverse osmosis, ultrafiltration and gas permeation.

The most important membrane qualities are:

1. High selectivity.

2. High permeability.

3. Mechanical stability.

4. Temperature stability.

5. Chemical resistance.

Selectivity is placed first in the list as low permeability can be compensated to a certain extent by an increase in membrane surface area, whereas low selectivity leads to multi-stage processes, which in most cases are not economical compared with established conventional processes.

One of the oldest and important membrane material, cellulose acetate or cellulose triacetate is still of prime importance in reverse osmosis, ultrafiltration and gas permeation, despite restrictions regarding temperature and pH.

Figure 6.2 classifies membranes according to structure, production, essential transport mechanism and areas of application.

6.5 Reverse Osmosis for Regeneration

The phenomenon of osmosis is the process of a solvent diffusing through a membrane which is permeable to it but which is impermeable to the chemical species which make up the solute. The phenomenon exists because of the inequality of the chemical potential of water in the pure liquid state and in the mixture. We have the relation for chemical potential of a substance i in an ideal solution, and is given as [24],

$$\mu_i = \mu_i^{\circ} + RT \ln x_i \tag{6.1}$$

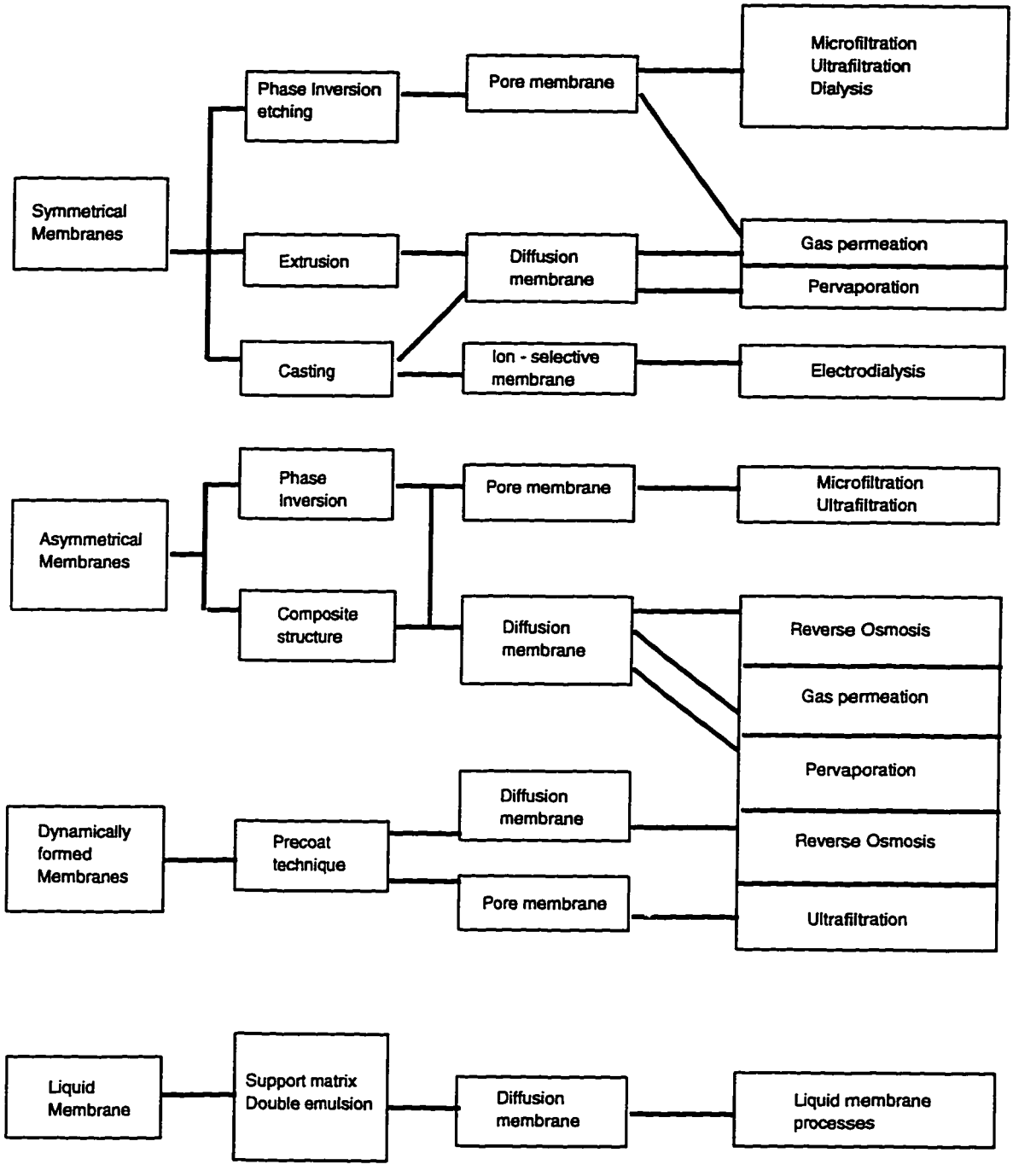

Figure 6.2: Membrane classifications.

It is easily seen that chemical potential in the solution is lower than the chemical potential in the pure state, because of its smaller mole fraction. Chemical species diffuses from region of higher to lower chemical potential. Thus the pure water will diffuse into the weak desiccant raising its chemical potential.

6.6 Evaluation of the Osmotic Pressure

The passage of water through the membrane can be prevented if the chemical potential of the weak desiccant can be increased to the same value as that of the pure water at temperature, T and pressure P_o.

As is evident from equation (3.9) that μ_i always increases with increasing pressure. Therefore, an increase in μ_i in the weak desiccant can be achieved by increasing the total pressure on the weak desiccant side. But the semi-permeable membrane must be strong enough to support this increase in pressure. The osmotic pressure is a function of the desiccant and is not a function of the nature of the membrane. The osmotic pressure Π, then, is defined as [24]

$$\Pi = P - P_o \tag{6.2}$$

where P is the pressure maintained on the weak desiccant at equilibrium.

The value of Π is ascertained in the following manner for an ideal solution. The chemical potential of the pure water at equilibrium is given by

$$\mu_i = \mu^{\pi}_{i,o} + RT \ln x_i \tag{6.3}$$

where x_i is unity and $\mu^{\pi}_{i,o}$ is a reference value for pure water measured at pressure P_o. For the weak desiccant in equilibrium with the pure water

$$\mu_i = \mu^{\pi}_i + RT \ln x_i \tag{6.4}$$

where μ^{π}_i is a reference value measured for pure water at the pressure P and the same temperature. Upon equating these two equations, one finds that

$$\mu^{\pi}_{i,o} = \mu^{\pi}_i + RT \ln x_i \tag{6.5}$$

or

$$RT \ln x_i = \mu^{\pi}_{i,o} - \mu^{\pi}_i \tag{6.6}$$

The quantity $\left(\mu^{\pi}_{i,o} - \mu^{\pi}_i\right)$ represents the change in g (Gibbs energy) for the pure substance at constant temperature as the pressure is altered from P to P_o. For a pure substance,

$$dg = vdP - sdT \tag{6.7}$$

Therefore for a pure water,

$$d\mu_T = dg_T = vdP \tag{6.8}$$

Thus

$$\left(\mu_{i,o}^{-} - \mu_i^{-}\right) = \int_P^{P_o} vdP \tag{6.9}$$

where v is the specific volume of the pure water. The volume of the liquid is assumed to be independent of pressure. Subsequent integration of equation (6.9) and substitution in equation (6.7) yields,

$$RT \ln x_i = v\left(P_o - P\right) \tag{6.10}$$

or on the basis of the definition of the osmotic pressure,

$$\Pi = P - P_o = -\frac{RT \ln x_i}{v} \tag{6.11}$$

If x_N represents the mole fraction of the total desiccant dissolved in the water, then

$$\Pi = -\frac{RT}{v} \ln\left(1 - x_N\right) \tag{6.12}$$

Chapter 7

Results and Discussions

In this chapter the results of different topics viz., desiccant and desiccant mixtures, pipeline drying and regeneration of liquid desiccants are discussed.

7.1 Desiccants and Desiccant Mixtures

Although several types of desiccants are used for industrial applications, lithium chloride and calcium chloride are commonly used in solar applications. Before conducting the thermodynamic analysis of liquid desiccants, an attempt was made to collect the properties currently available for these desiccants. Table 7.1 compares the partial pressure of water vapor over lithium chloride solution measured at 20% concentration from [6] and [28]. It is interesting to note that the deviation varies from 2 to 20% with Ertas et al.[6] result is taken as the base.

Table 7.1: Vapor pressure data for lithium chloride, in mm Hg.

Temperature, ^{o}C	Ertas et al. [6]	Uemura [28]	% Deviation
26.66	23	18.36	20.20
32.22	29	25.41	12.38
37.77	39	34.83	10.7
43.33	52	47.27	9.12
48.88	68	63.29	6.92
54.44	89	83.59	6.08
60.00	111	108.7	2.04

The deviation may be mainly due to the purity of the desiccant. Further, it can be seen that the deviation is large at low temperatures and as the temperature increases the deviation decreases. The same conclusion is drawn when we compared the partial pressure of water vapor of calcium chloride taken from [6] and [29]. In this case, the deviation varies from about 7 to 31 % as shown in Table 7.2. In different countries, desiccants are available in different forms with different purities. Since vapor pressure is one of the important properties in air dehumidification, an attempt is made to predict this property based on classical thermodynamics approach. It is to be noted from eqn (3.29) that activity coefficient is needed for vapor pressure calculation. Since this value is readily available for lithium chloride [13], the analysis is carried out only for this desiccant. However, the analysis can be extended to any desiccant.

Table 7.2: Vapor pressure data for calcium chloride, in mm Hg.

Temperature, ^oC	Ertas et al. [6]	Dow Chemical [29]	% Deviation
26.66	37	25.52	31.02
32.22	43	33.83	21.32
37.77	57	45.264	20.59
43.33	72	60.68	15.73
48.88	93	80.84	13.07
54.44	117	106.7	8.84
60.00	149	138.9	6.77

Thermodynamics of equilibrium is used to calculate the vapor pressure of lithium chloride over its solution. The following assumptions are made in the present analysis:

(1) The activity coefficient is assumed to be constant with respect to the temperature and

(2) The water vapor is assumed to behave as an ideal gas.

Figure 7.1 shows the comparison of computed vapor pressure of lithium chloride at 20% concentration with values given by Ertas et al. [6] and Uemura [28]. The present analysis agrees very well with the results of Uemura [28] but predicts value lower by $4-10\%$ than Ertas et al.[6]. The deviation may be due to the purity of the desiccant used by Ertas et al. [6]. Thus the present analysis gives the confidence in calculating the vapor pressure of the desiccant.

Figure 7.2 shows the calculated partial pressure of water vapor over lithium chloride solution at 5 - 20% with an increment of 5% concentration by the present analysis and compared with the results given by Uemura [28]. The agreement is very good and the slight deviation may be due to the assumptions made in the present analysis.

Vapor pressure of the lithium chloride is also calculated at higher concentrations, that is, at 25 - 40% with an increment of 5% of the desiccant. At all these concentrations good agreement between the experimental and the results of the present analysis is observed. It is seen from the Fig. 7.3, at high concentrations the deviation

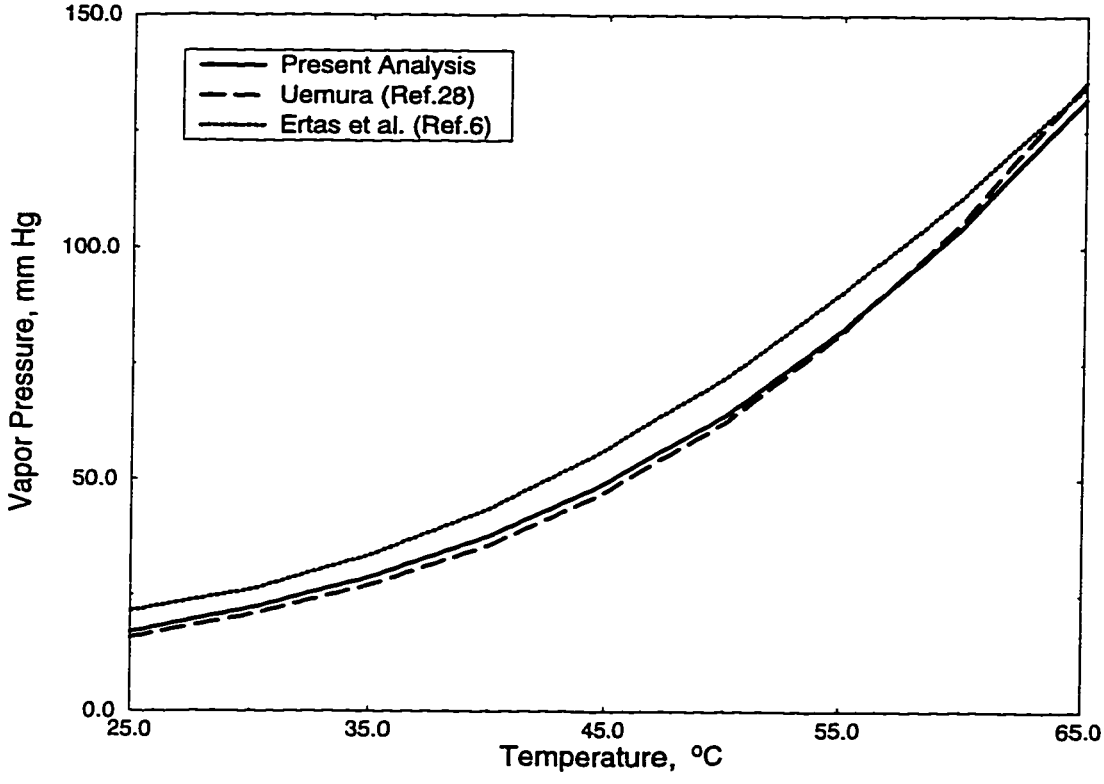

Figure 7.1: Comparison of vapor pressure of LiCl at 20% concentration.

increases and the deviation is negligible at low temperature but as the temperature increases the deviation also increases with increase in concentration. This can be explained by the fact that in the present analysis, the activity coefficient is assumed to be constant. It seems at higher concentrations, the activity coefficient may be a function of temperature as well as concentration.

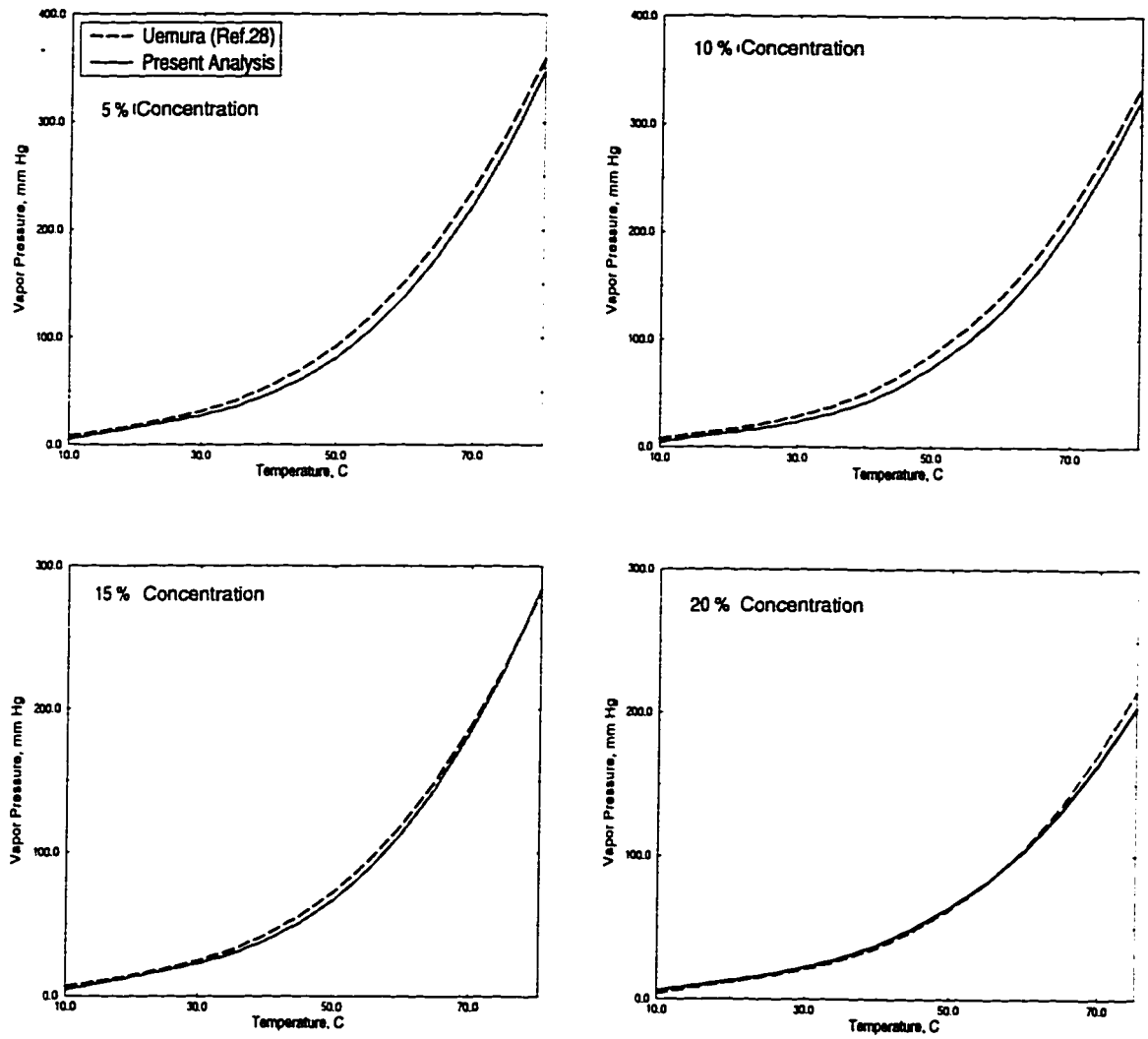

Figure 7.2: Comparison of vapor pressure of LiCl at different concentrations.

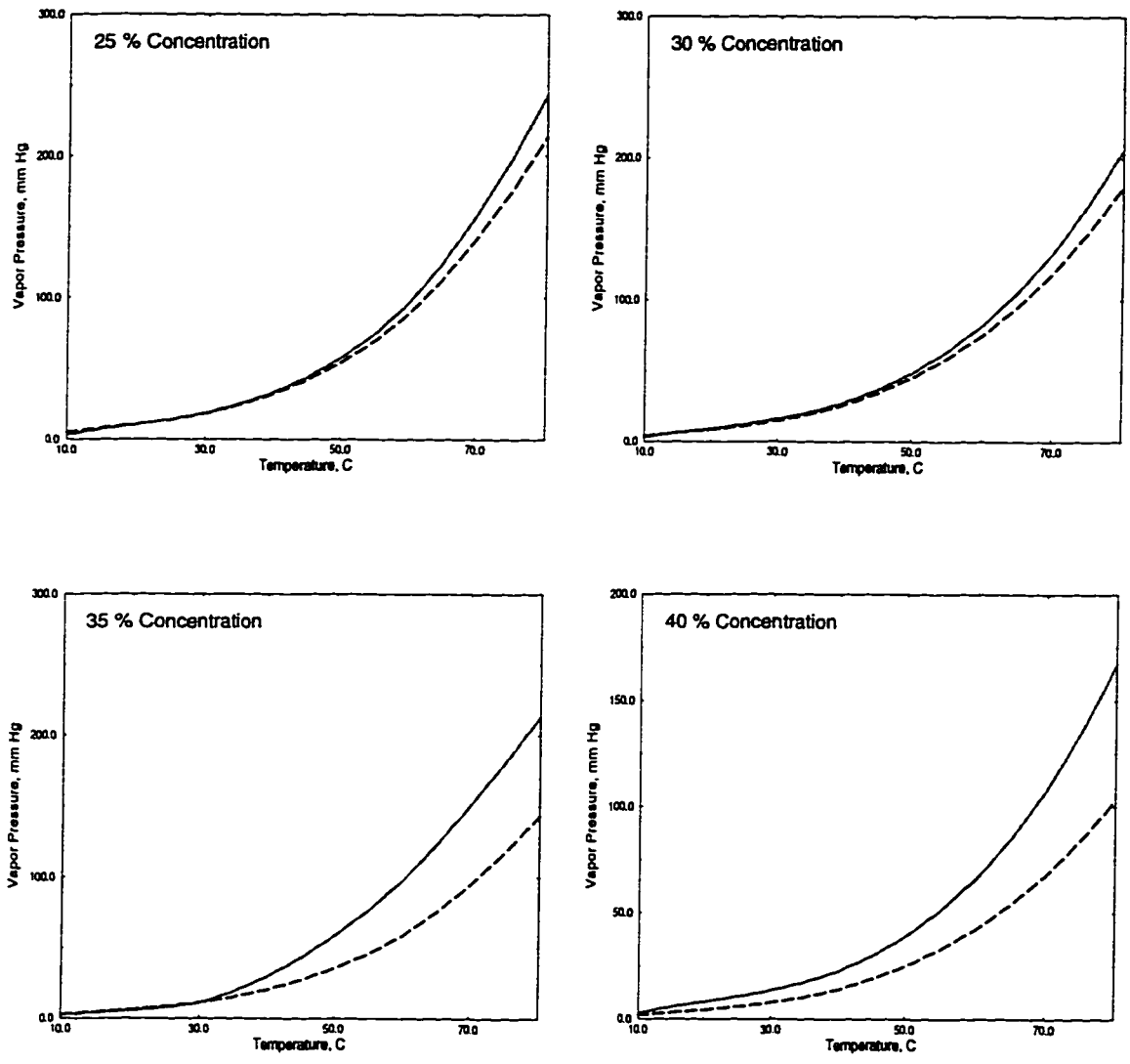

Figure 7.3: Comparison of vapor pressure of LiCl at different concentrations.

Simple mixing rules are used to predict the thermophysical properties such as vapor pressure, density, and viscosity of mixture of lithium chloride and calcium chloride for different concentrations. In the calculation of these properties of mixtures, 50% concentration of each desiccant is assumed. These properties are evaluated with and without using the interaction parameter as given in equations(4.1) and (4.4) respectively. The interaction parameter is taken as the product of the weight fraction of the desiccants. The density of mixture of lithium chloride and calcium chloride at 30, 35 and 40% overall concentration with 50% concentration of each component as calculated by the present analysis is compared with experimental results and is shown in Fig. 7.4. At first calculations are made at 30% concentration and as shown in this figure that a good agreement between the results of experimental and the present analysis without interaction parameter is observed. It is clear that the inclusion of the interaction parameter in the present analysis does not work well for the calculation of density of the mixture of desiccants. To study the effect of interaction parameter at higher concentrations, analysis is extended to find the density of mixture at 35% and 40% concentrations. As at 30% concentration, the inclusion of interaction parameter does not work well at higher concentrations also as shown in the figure.

Figure 7.5 shows the comparison of viscosity of the desiccant mixture at 30, 35 and 40% overall concentration with 50% concentration of each component. Calculations are made with and without the interaction parameter. It can be seen from

this figure that the values calculated using interaction parameter is close to the experimental values of Ertas et al.[6]. Therefore, in the calculation of viscosity the inclusion of interaction parameter works well at all these concentrations.

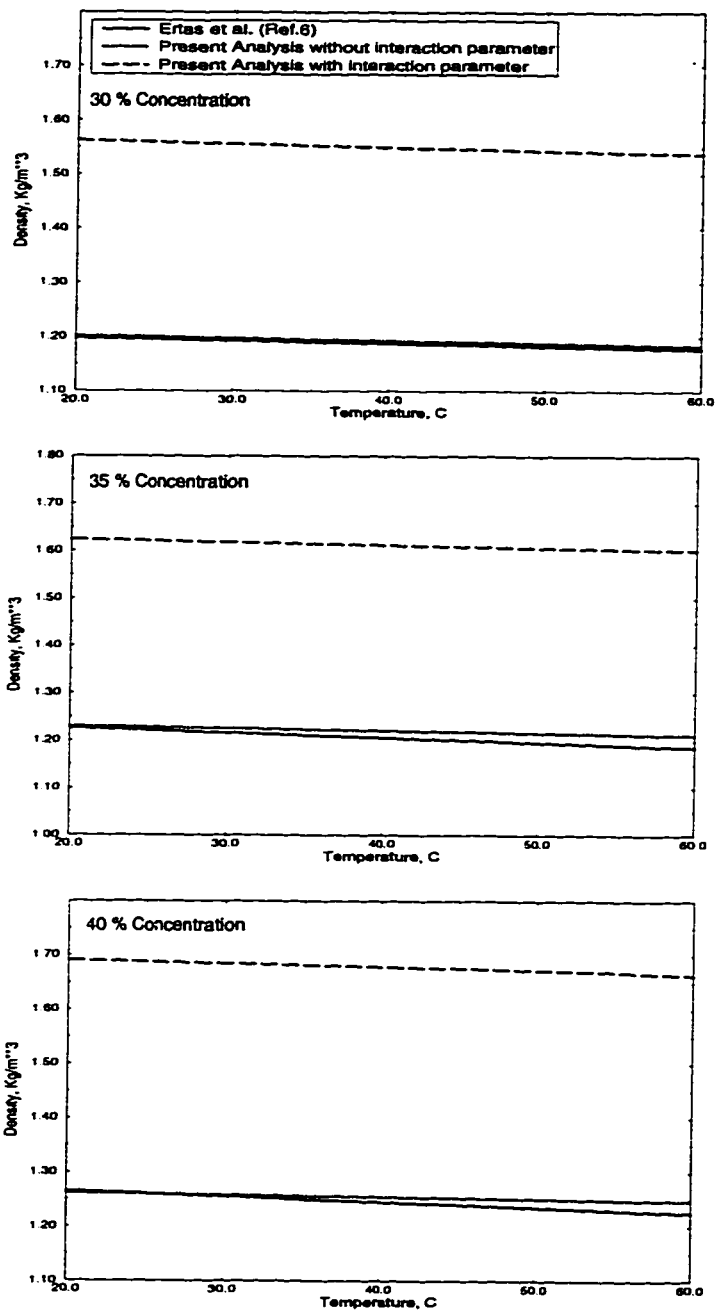

Figure 7.4: Density of LiCl and $CaCl_2$ mixture at different concentrations.

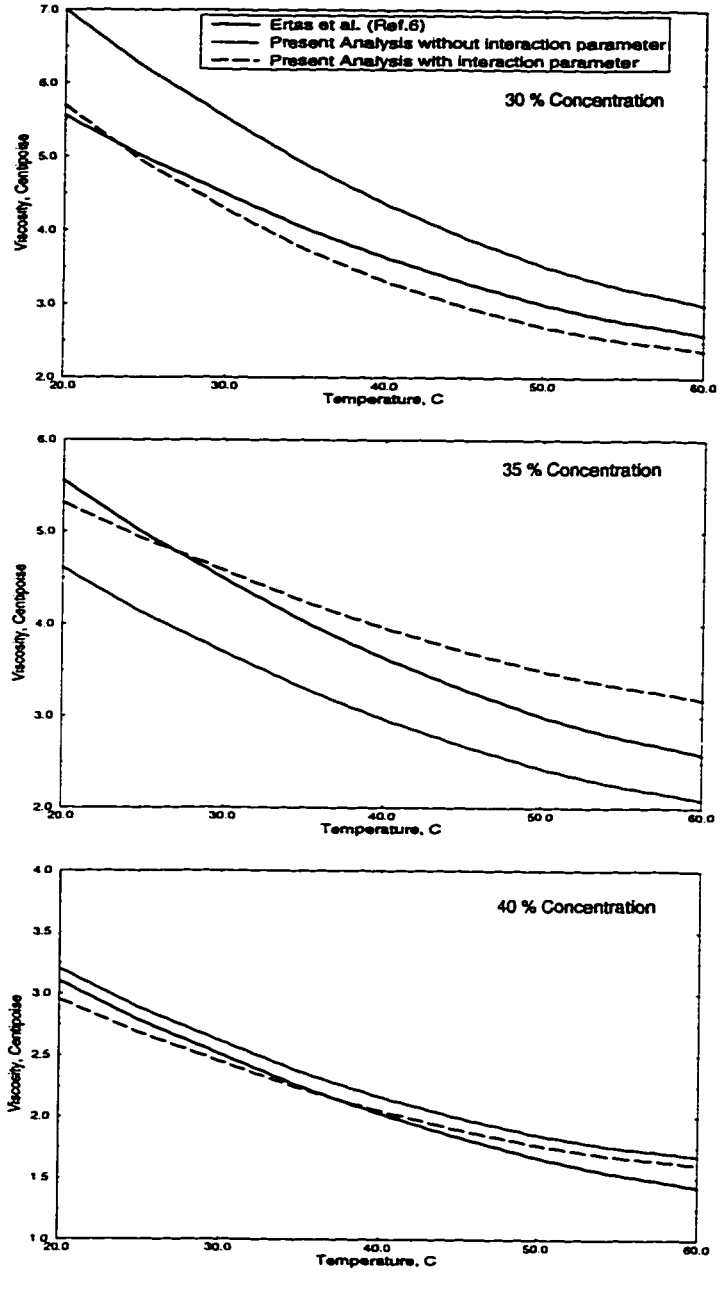

Figure 7.5: Viscosity of LiCl and $CaCl_2$ mixture at different concentrations.

Figure 7.6 shows the comparison of vapor pressure of the desiccant mixture between experimental and present analysis at 20, 30 and 40% overall concentration with 50% concentration of each component. Calculations are made with and without using the interaction parameter. It can be seen from the figure that the values of vapor pressure calculated without using the interaction parameter are close to the experimental results of Ertas et al [6]. Therefore, it can be said that like the density where interaction parameter does not work well, so also for vapor pressure.

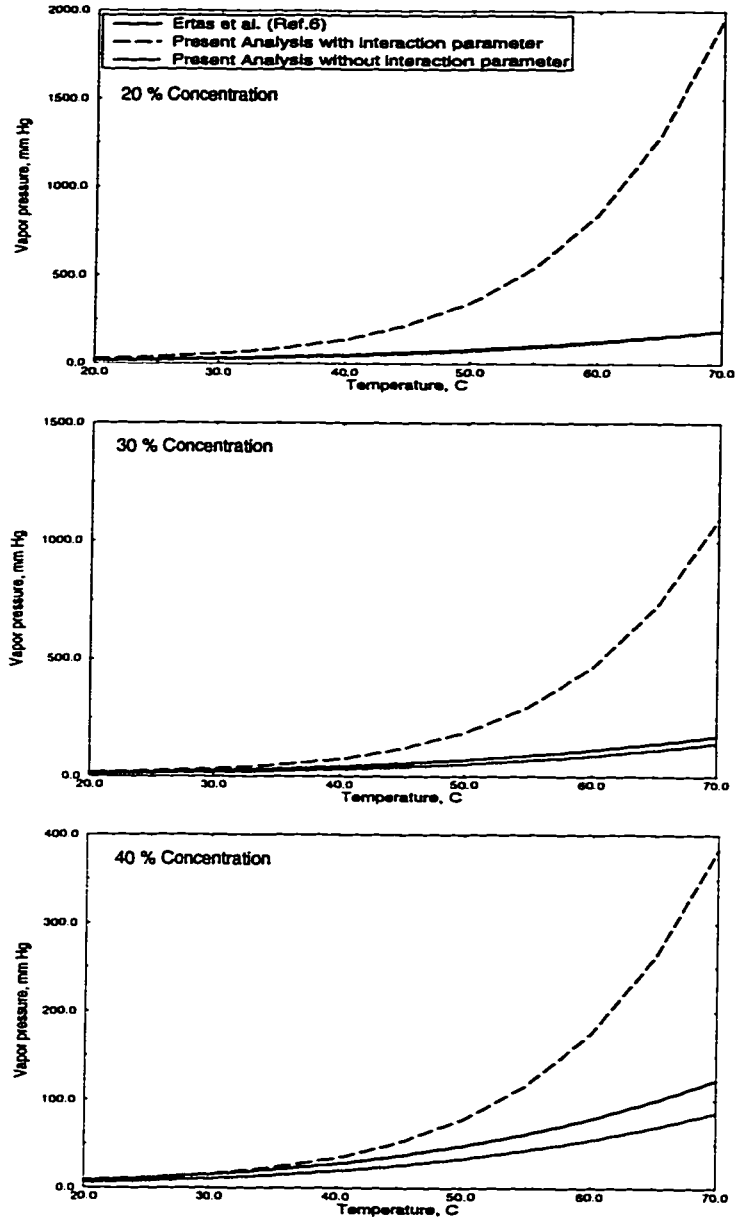

Figure 7.6: Vapor pressure of LiCl and $CaCl_2$ mixture at different concentrations.

7.2 Pipeline Drying

In order to predict the drying time required to dry the pipeline of given length for different operating parameters, both analytical as well as the numerical methods are studied. Analytical results are compared with the numerical analysis at short length of pipeline. It is found appropriate to compare these two results since both solutions are obtained with the same operating parameters. Table 7.3 summarizes the pipeline dimensions and different operating parameters.

Table 7.3: Pipeline dimensions and operating parameters.

Pipeline Diameter (D)	460 mm
Ambient Temperature	20 ^oC
Dry air entrance temperature	15 ^oC
Inlet pressure (P_i)	5 bar
Outlet pressure (P_o)	1 bar
Volumetric flow rate of dry air (Vfr)	$5000 - 15000\ m^3/h$
Length of pipeline (L)	$50 - 150\ km$
Water film thickness	$50 - 100\ \mu m$
Dry air dew point temperature (T_{dp})	$-20\ ^oC$ - $-40\ ^oC$

Figure ?? illustrates the dynamics of the drying process and it shows the variation of water vapor concentration in dry air as it travels along the pipeline. It can be seen that the change in the concentration is rapid at the entrance of the pipeline. This can be explained by the fact that near the entrance the evaporation of moisture from the pipe wall occurs very rapidly due to the large difference between the concentration of water vapor near the pipe wall and the air stream until it gets saturated as shown by a horizontal line.

In order to determine the effect of various operating parameters on the process of pipeline drying, a parametric study is conducted using the analytical method. The study is initiated by predicting the behavior of the drying process under the influence of ambient temperature and the water film thickness. It is evident from Fig. 7.8 that the drying time increases with the increase in water film thickness but decreases with the increase in ambient temperature. This may be attributed to the fact that as the ambient temperature increases potential for mass transfer from the water film to the air increases and hence the drying time decreases.

Figure 7.9 shows the variation in drying behavior as a function of volumetric flow rate with the dew point temperature as a parameter. It can be seen from the figure that as the dew point temperature of dry air is decreased from $-20\ ^{o}C$ to $-30\ ^{o}C$ and $-40\ ^{o}C$ the drying time is reduced and the behavior at these temperatures becomes closer to each other because of the higher level of dryness. This can be explained by the fact that the potential for mass transfer increases with decrease in

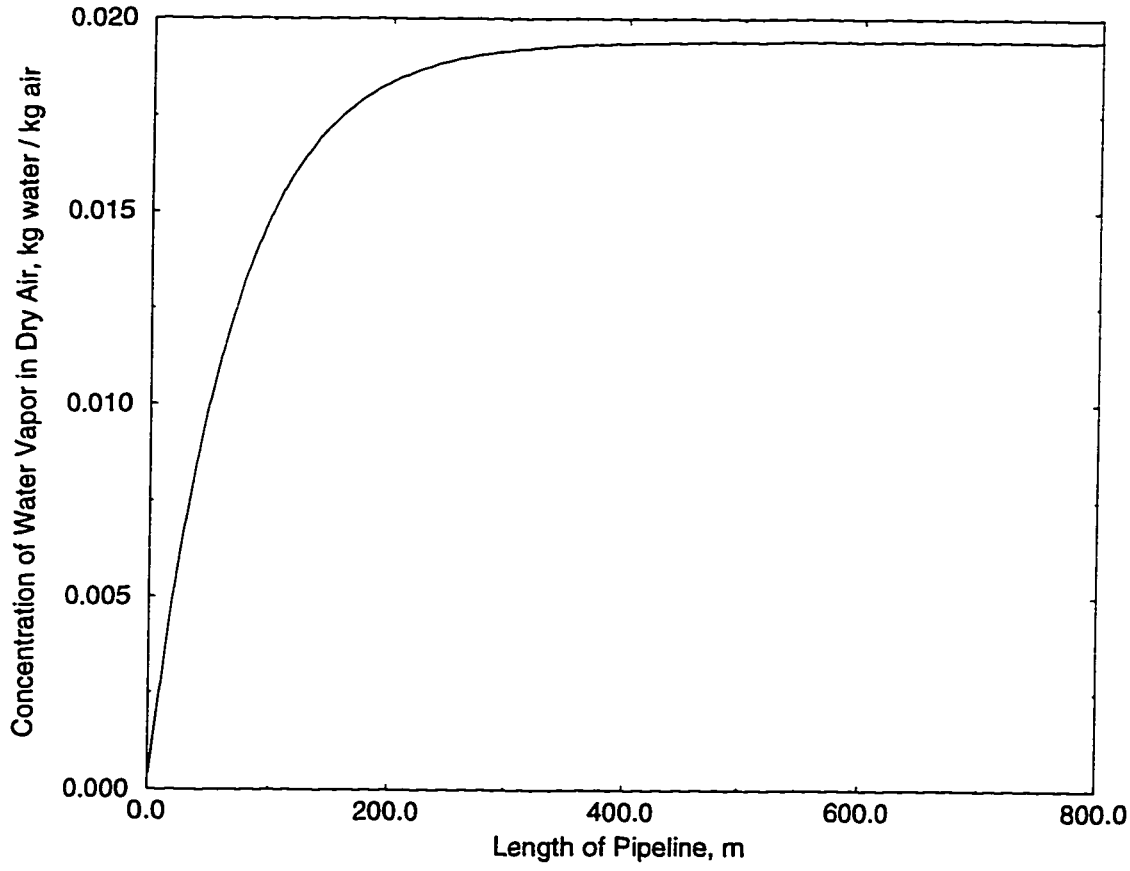

Figure 7.7: Concentration variation for a 800 m pipeline at 20th minute

air dew point temperatures as evident from the figure.

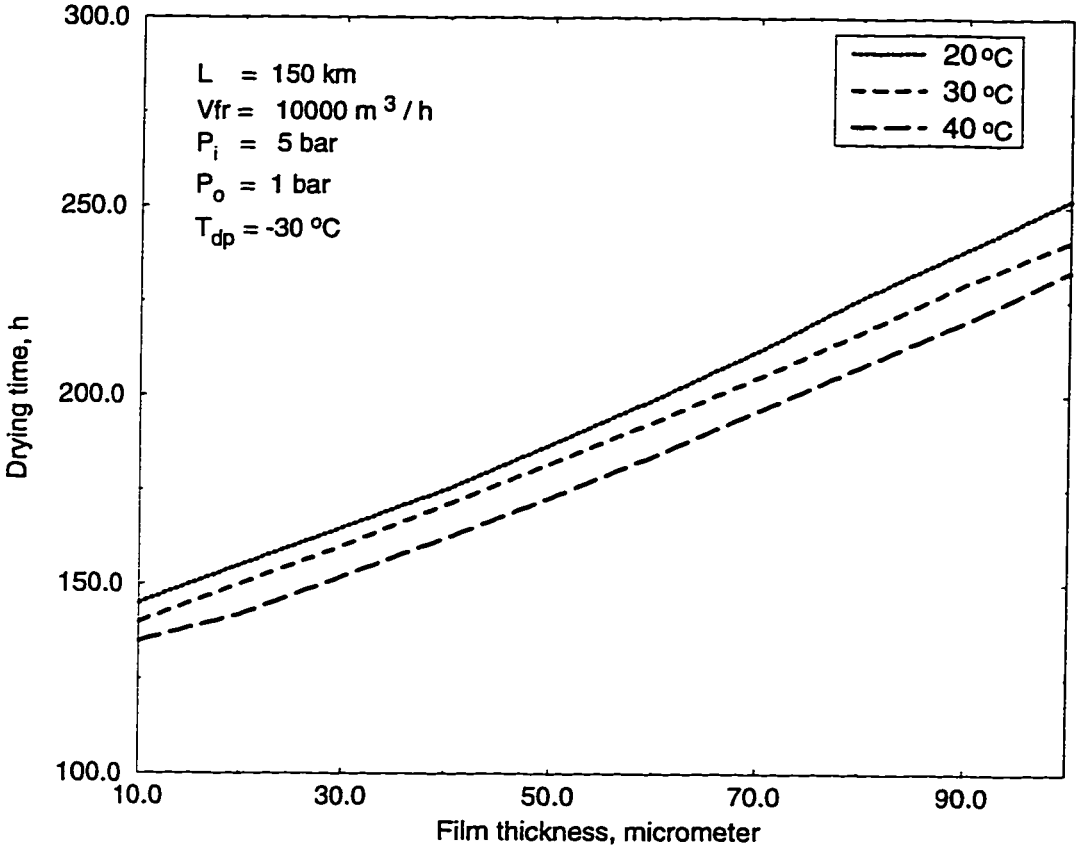

Figure 7.8: Effect of volumetric flow rate and the dew point temperature on drying time.

In Fig. 7.10, the effect of length of pipeline and the air dew point temperature on the history of the drying process is shown. As illustrated in Fig. 7.10 that the drying process is continous in the sense that the pipeline is dried from its initial moisture content to the final value with a constant rate period. As expected, with an increase in the length of pipe, the duration of the total drying period increases.

To facilitate the availability of the ready made equations in the industry for the prediction of drying process, correlations are developed which give the values of drying time required at different operating parameters. This correlations are given in the Appendix.

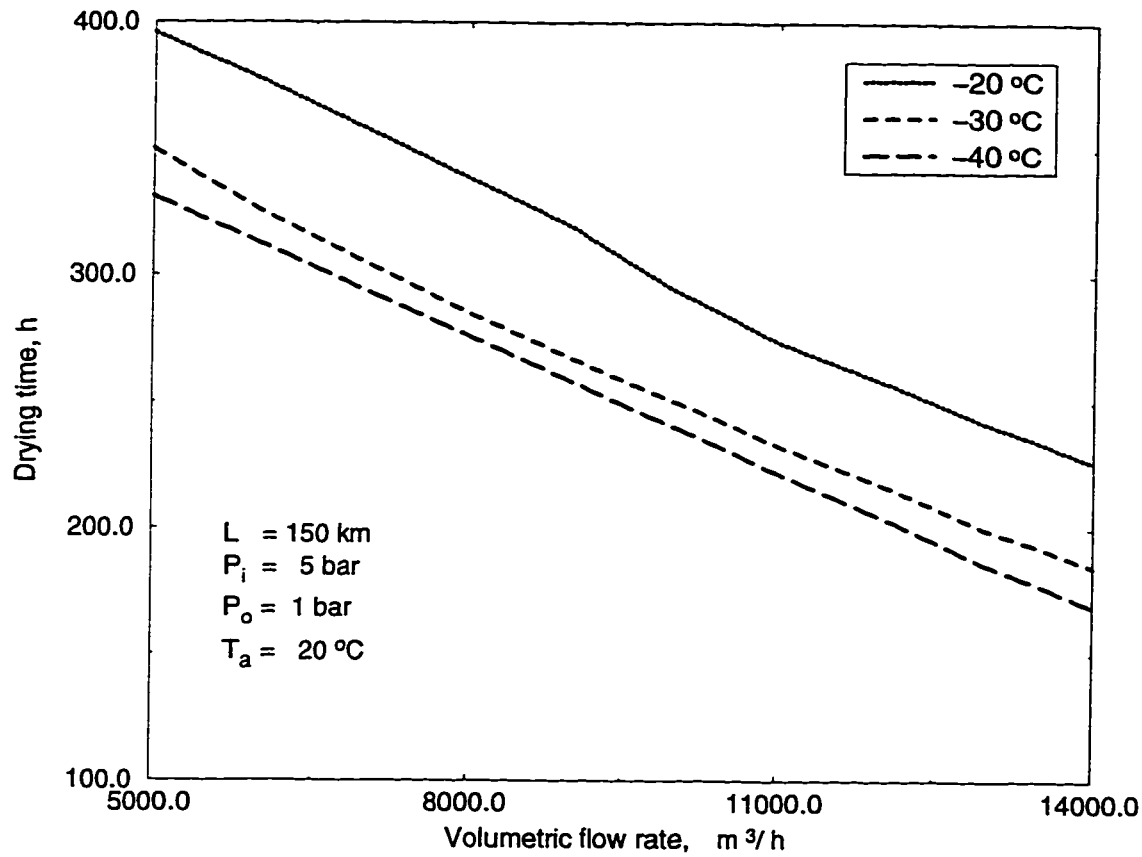

Figure 7.9: Effect of ambient temperature and the water film thickness on drying time.

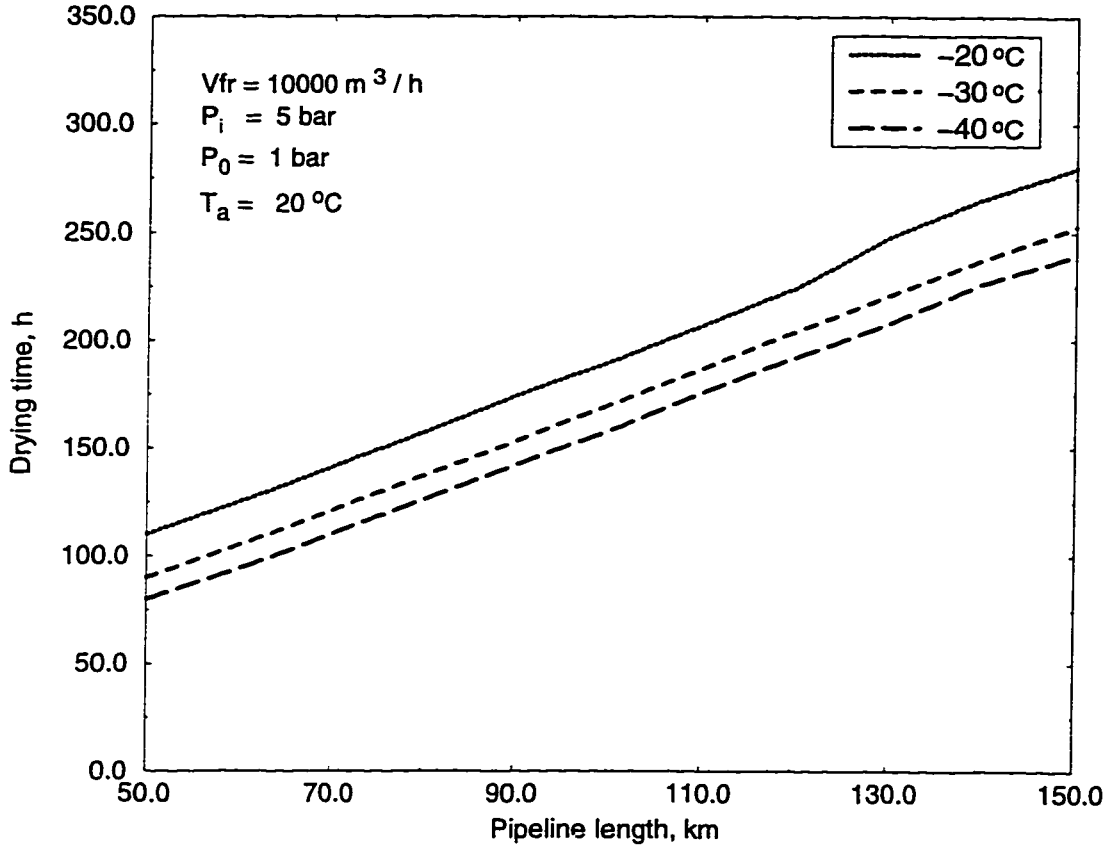

Figure 7.10: Effect of pipeline length and the dew point temperature on drying time.

The calculations made with variation of different operating parameters characterizing the drying process show that the process of ventilative drying of a pipeline is , under certain conditions, a very competitive means of removing the moisture left over in the pipeline.

As mentioned earlier that in the present analysis all the results obtained are under the assumption that the dry air temperature does not change as it travels along the pipeline. Due to this assumption, there is a slight difference in the drying time as calculated by Battara [19]. However, allowing for the temperature drop of the desiccant in the evaporation section enables one to predict the drying time more accurately, but it consumes more computer time. At the same time, neglecting this, results in an error not exceeding 10% in predicting the drying time.

In order to evaluate the accuracy of the numerical analysis formulation the present solution is compared with the analytical results.

Figure 7.11 compares the present numerical solution with the analytical solution for a pipeline of length $20m$ at the specified operating parameters. It is evident from the figure that the results obtained from both the analysis for the concentration variation of dry air is comparable at short lengths of pipeline. The numerical analysis is carried out for short length because, in the case of ventilative drying the special stability condition equation (5.48) is imposed on the solution of equations (5.40 - 5.42), which limits the choice of h, the spatial step. This is explained by the fact that evaporation of the moisture from the pipe wall occurs very rapidly due to the

large difference in the concentration. And, if a fairly large spatial step is chosen, the dry air may already reach the saturated state in the first spatial step, and this may occur at any point of this step, depending on the evaporation rate and the chosen length of the step. The spatial step must therefore be chosen so as to eliminate this situation.

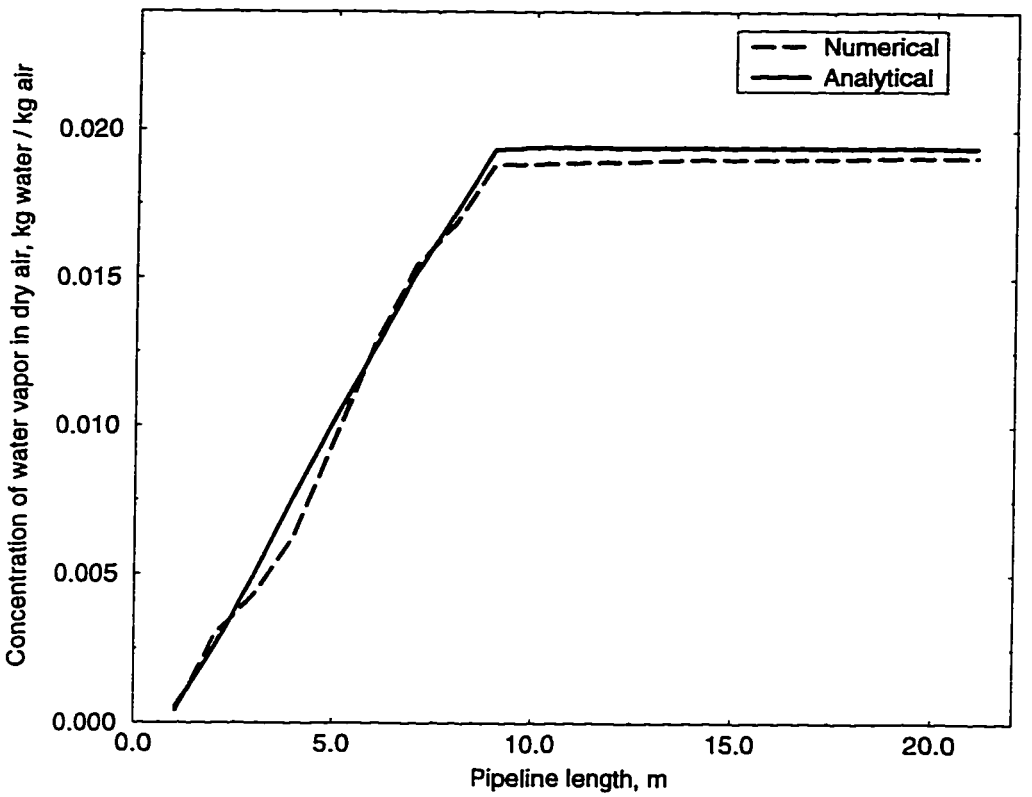

Figure 7.11: Concentration variation for a 20 m pipeline as a function of pipe length at 55th second.

7.3 Regeneration of Liquid Desiccants

In order to predict the pressure required to regenerate the weak desiccant from a given concentration to a required concentration, an analytical method is studied. It is assumed that the two sections as shown in Fig. 6.1 are initially at atmospheric conditions. Effect of temperature and the concentration on the osmotic pressure required are plotted for two different desiccants, that is lithium chloride and calcium chloride.

Figure 7.12 illustrates the variation of pressure for different temperatures and concentrations of lithium chloride solution. It can be seen from the figure that the effect of temperature is negligible at low concentrations. However, this effect is significant at higher temperatures and concentrations.

Figure 7.13 shows the effect of the temperature and the concentration on the pressure required to regenerate the weak desiccant of calcium chloride. The same trend for the pressure required is observed for calcium chloride also. It can also be seen that the pressure required in the case of calcium chloride is much less than that of lithium chloride for the same specified temperature and concentration.

In both the figures 7.12 and 7.13 shown above, the pressure in MPa represents the pressure which has to be maintained across the semipermeable membrane so that condition of equilibrium can be established between the two sections as shown in Fig 6.1. At this condition there will not be any diffusion from either of the sections. If a

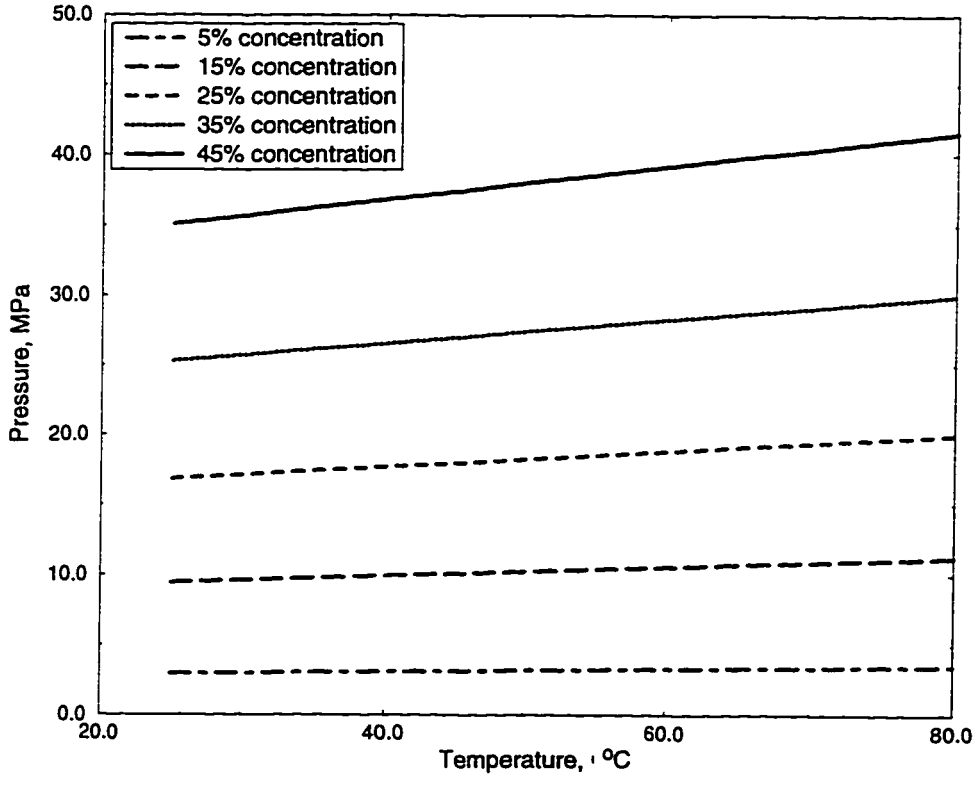

Figure 7.12: Pressure required for regeneration of lithium chloride solution at different concentration.

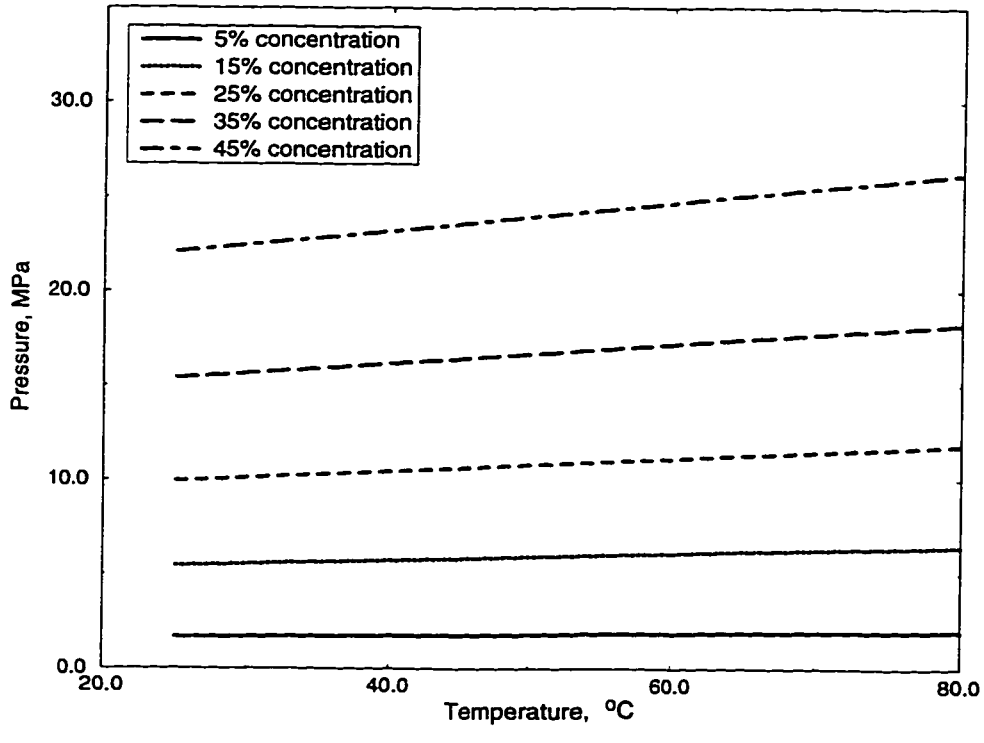

Figure 7.13: Pressure required for regeneration of calcium chloride solution at different concentration.

pressure less than the osmotic pressure is maintained, then the pure water will flow through the membrane because of high chemical potential of the pure solvent. If pressure applied is increased in the desiccant section more than the osmotic pressure results in greater chemical potential. Therefore, instead of the normal behavior of diffusion from the pure solvent section to the desiccant section, flow will take place from the desiccant section to the pure solvent, thereby making the desiccant more concentrated.

Correlations are developed that give the pressure required to regenerate the weak desiccant for different temperatures and concentrations and they are given in the Appendix.

Chapter 8

Conclusions

8.1 Conclusions

The classical thermodynamics approach was used to predict the vapor pressure of a desiccant namely lithium chloride using activity coefficient. The predicted values agree very well with the experimental results found in the literature. The thermophysical properties such as vapor pressure, density, and viscosity of the desiccant mixtures namely lithium chloride and calcium chloride were estimated using the simple mixing rules and compared with the only available experimental results of these properties for this mixture. It is found that the inclusion of the interaction parameter works very well for calculating the viscosity of the desiccant mixture and not so well for density and vapor pressure of the desiccant mixture.

Drying with dry air is one of the most widely used methods for removing residual

water after the hydrostatic testing. The problem of pipeline drying was solved using the analytical and numerical methods. Analytical method using Laplace transforms is used to find the drying time required to dry a pipeline of $150km$ length. However, numerical method is also used, but for predicting the drying time for a length of upto 20 m and the results obtained by these two methods show good agreement. In many cases, the dry air process proves to be highly competitive and allows the fundamental parameters to be optimized in addition it offers the following advantages.

1. The equipment cost is relatively low.

2. It enables attaining very high drying levels.

3. It does not require skilled personnel.

Reverse osmosis has been used for predicting the pressure required to regenerate the weak desiccant solution of lithium chloride and calcium chloride for different temperatures. Corellations are also derived for predicting the pressure required to regenerate weak desiccant from a given concentration to a required concentration. It is concluded from the analysis that the pressure required to regenerate calcium chloride is less than that of lithium chloride.

8.2 Recommendations

- Vapor pressure of other desiccants can also be found using the vapor - liquid

equilibrium.

- Desiccants other than lithium chloride and calcium chloride should be tried to find the properties of mixtures which are both cost effective and efficient.
- The effect of temperature drop of the inlet dry air can be studied.
- Effect of temperature at higher concentrations on activity coefficient can be studied.

APPENDIX

Correlations for Regeneration Process

Lithium Chloride

$$P = -5.44415 + .870007 * C + \frac{T}{15.844}$$

for the concentration range $5 - 45$ %

and temperature range $25 - 80\ ^oC$

Calcium Chloride

$$P = -4.5085 + .551657 * C + \frac{T}{18.67}$$

for the concentration range $5 - 45$ %

and temperature range $25 - 80\ ^oC$

Where C is the desiccant concentration and P is pressure in MPa.

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